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# **NIST Calibration Services for Humidity Measurement**

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## NIST HUMIDITY CALIBRATION SERVICES

The National Institute of Standards and Technology (NIST), formerly National Bureau of Standards (NBS), provides a service to Government agencies and to the public for the calibration of humidity measuring instruments. Calibrations are performed by subjecting the instrument under test to atmospheres of known moisture content produced by the NBS two-pressure humidity generator. The most accurate calibrations are made with the NBS standard hygrometer, a device based on the gravimetric method. The discussion that follows is broken into two separate parts. Part A describes the NBS standard hygrometer. It is based almost entirely on a 1964 publication [Ref. 1]. Pertinent parts are reproduced here. Refer to [1] as indicated below for more details, including many references. Part B describes the NBS two-pressure humidity generator.

Among the contributors, A. Wexler and S. Hasegawa are retired from NIST. They have made significant contributions to the original work on the NBS standard hygrometer and the NBS two-pressure humidity generator, respectively. P. H. Huang has edited this report by shortening the original papers of A. Wexler, R. W. Hyland, and S. Hasegawa in order to provide a more convenient reference for the two original lengthy papers.

### A. NBS STANDARD HYGROMETER

The NBS standard hygrometer [1] is based on the gravimetric method of moisture determination. The measuring operation involves the absorption of the water vapor from a water vapor-gas mixture by a solid desiccant and the determination of the mass of this water vapor by precision weighing; it also involves the determination of the mass of the associated gas of known density by counting the fillings of two calibrated stainless steel cylinders.

A sample of test gas of constant moisture content from the NBS two-pressure humidity generator is allowed to flow through the NBS standard hygrometer and the instrument under calibration. At the termination of a run, the mass of water vapor removed by the drying train is determined by precision weighing. The drying train consists of three interchangeable glass absorption U-tubes filled with anhydrous magnesium perchlorate and phosphorous pentoxide. The total volume of dry gas is measured by counting the number of times two calibrated cylinders, each of about  $.03 \text{ m}^3$  capacity, are alternately evacuated and filled with the dry gas. By means of a pressure switch, a vacuum pump, and associated automatic controls, each of the two cylinders is evacuated and filled to a preset pressure, producing a continuous flow of test gas. The cylinders are immersed in a thermostated oil bath. After each filling, the gas collected in a cylinder is allowed to reach equilibrium and then the gas pressure and temperature are measured. The mass of the dry gas is obtained by multiplying the volume by the appropriate gas density.

An analysis of the random and systematic errors affecting the overall accuracy in the determination of mixing ratio (mass of water vapor/unit mass of dry gas) shows that if 0.60 gram(g) of water vapor is collected from moist air, then the estimated maximum uncertainty expected for mixing ratios between



27 mg/g and 0.19 mg/g is 12.7 parts in  $10^4$ .

#### A-1 COMPUTATIONS, CORRECTIONS, SOURCES OF ERROR, AND ACCURACY/PRECISION

Mixing ratio is defined by the equation

$$r = M/(V\rho)_{t,B} \quad (1)$$

where

- r = mixing ratio, mass of water vapor per unit mass of dry gas, g/g
- M = mass of water vapor, g,
- V = volume of the dry gas associated with the mass of water vapor,  $\text{cm}^3$  at temperature t and pressure B, and
- $\rho$  = density of the dry gas associated with the mass of water vapor,  $\text{g/cm}^3$  at the temperature t and pressure B.

The subscripts t and B merely emphasize the pressure-temperature dependence of the density and volume, and will not appear in subsequent sections. The mixing ratio is a computed quantity whose magnitude is the ratio of two measurable quantities - the mass of water in a given water vapor-gas sample and the associated mass of dry gas. The mass of water is determined directly by weighing. The mass of dry gas is determined indirectly through a measurement of its volume and a knowledge of its density.

Each of the measurements contributing to the value of the mixing ratio as determined by use of the gravimetric hygrometer was considered in detail in [1] and what follows is a summary of that error analysis.

##### A-1-1 BASIS AND NOMENCLATURE OF ESTIMATES OF ACCURACY

Although an attempt was made to eliminate or reduce to a negligible value all known sources of systematic error, there remain several that contribute to the uncertainty in the mixing ratio. The nature and magnitude of these will be assessed. All other errors are assumed to be random and are treated as such. The estimate of the accuracy with which the gravimetric hygrometer can measure the mixing ratio of a gas sample is based on both the systematic and random errors. Standard deviations are computed and used as a measure of the random errors. Since the mixing ratio is a computed quantity, the law of propagation of errors [2] is applied to the random errors and the standard deviation for the mixing ratio  $s(r)$  is given by eq. (2) (see [1] pp. 397-398). The standard deviation of any parameters, z, is expressed as  $s(z)$ .

$$s(r) = \left[ \left( \frac{\partial r}{\partial M} \right)^2 s^2(M) + \left( \frac{\partial r}{\partial V} \right)^2 s^2(V) + \left( \frac{\partial r}{\partial \rho} \right)^2 s^2(\rho) \right]^{1/2} \quad (2)$$

Maximum random errors will be assigned as 3 standard deviations, and, conversely, if a maximum random error is obtained, its standard deviation will be assigned as 1/3 of the maximum.

##### A-1-2 MEASUREMENT OF THE MASS OF WATER COLLECTED IN U-TUBES

The mass of the water absorbed by the desiccant in a U-tube is weighed against a tare tube of similar size, weight and shape on an equal arm balance. It depends not only on the values of the weights used in the initial and final weighings but also on such factors as the air buoyancy effect on the U-tube, tare and weights; the water vapor adsorption on the external surfaces of the U-tube; tare and weights; static charge on the U-tube and tare; convective air currents within the balance case; handling and treatment of the U-tube and tare; mass of internal gas in the U-tube; and incompleteness of absorption by the desiccant. The mass of water vapor,  $M$ , absorbed by the desiccant in a U-tube is given by

$$M = W_f - W_i + C_w + C_b + C_a + C_g + C_i , \quad (3)$$

where

- $W_f$  = sum of face values of weights necessary to bring the balance to equilibrium after an experiment, with the U-tube on one pan and the tare on the other pan, g,
- $W_i$  = sum of face values of weights necessary to bring the balance to equilibrium before an experiment, with the U-tube on one pan and the tare on the other pan, g,
- $C_w$  = correction for calibration of weights, g,
- $C_b$  = correction for the effect of air buoyancy on U-tube, tare and weights, g,
- $C_a$  = correction for water vapor absorbed on external surfaces of U-tube, tare and weights, g,
- $C_g$  = correction for mass of gas sealed in the U-tube, g, and
- $C_i$  = correction for incompleteness of water vapor absorption by the desiccant, g.

The mass of water vapor,  $M$ , admixed with a given volume or mass of gas is the sum of the increases in masses of the first two tubes of the three-tube main absorption train, that is

$$M = m_1 + m_2 , \quad (4)$$

where

- $m_1$  = increase in mass of the first tube, g, and
- $m_2$  = increase in mass of the second tube, g.

The third tube is a guard against moisture entry from back streaming sources.

About 0.6 gram of water is collected in the first tube and 0.2 mg is collected in the second tube in a typical mixing ratio determination.

Each of the correction terms  $C_w$ ,  $C_b$ ,  $C_a$  and  $C_g$  given in eq. (3) is the difference between the corresponding correction for the initial and final weighings; for example,  $C_b = C_{bf} - C_{bi}$  where  $C_{bi}$  is a buoyancy correction applied to the initial weighing and  $C_{bf}$  is a buoyancy correction applied to the final weighing.

The sum of the corrections applied to the difference  $W_f - W_i$  for any tube is of the order of 2 mg. The corrections constitute nominally one-third of one percent of the total weight.

The standard deviation of M,  $s(M)$ , is

$$s(M) = [s^2(m_1) + s^2(m_2)]^{1/2} \quad (5)$$

The above corrections, the errors involved in applying these corrections, and uncertainties due to other factors are now discussed in detail (see [1] pp. 399-413).

A-1-2-1 Balance and Weights (see [1] p.399). The 100-gram capacity equal-arm semi-micro balance used to weigh the U-tubes has a reciprocal sensitivity of approximately 0.02 mg/division. It is possible to estimate to 0.1 division, that is, to the nearest 0.002 mg. Pointer deflections are observed through a telescope. The length ratio of the right to left balance arm is 1.000003. Single transposition weighings are used, which compensate for the inequality in armlength. Based on repeated weighing experiments with stainless steel weights of 50 and 100 grams, it is estimated that the variability of the balance, that is, the standard deviation of a single transposition weighing, is  $s(W_f) = s(W_i) = 0.011$  mg.

A set of class M weights [3] is used with the balance. The weights of face values 1 to 100 grams were fabricated from Brunton metal and have a stated density at 20°C of 7.89 g/cm<sup>3</sup>. The weights of face values 1 mg to 500 mg were fabricated from an alloy of 80 percent Ni and 20 percent Cr composition and have stated density at 20°C of 8.39 g/cm<sup>3</sup>. The maximum uncertainty in density is estimated to be 0.03 g/cm<sup>3</sup>. This contributes a systematic but negligible error.

The standard deviation of the correction for the calibration of the weights for the single weighing is nominally  $5.3 \times 10^{-6}$  g, and for a differential weighing  $s(C_w)$  is  $\sqrt{2}$  ( $5.3 \times 10^{-6}$ ) g or  $7.5 \times 10^{-6}$  g.

A-1-2-2 Buoyancy Correction (see [1] pp. 399-406). With an equal-arm balance, the use of a tare is normally the preferred procedure for precision differential weighing since it tends to compensate not only for the effect of air buoyancy on the U-tube and tare, but also for other possible changes in tube weight due to handling, dust accumulation, and moisture adsorption on the external surfaces. However, since the external volumes of the tare and U-tube are not precisely equal, and since barometric pressure changes may on occasion introduce significant density changes, a buoyancy correction is applied to the differential weighing. This correction is given by

$$C_b = \left[ \frac{W_{Lf}}{D_L} + \frac{W_{Sf}}{D_S} + V_U - V_T \right] \rho_f - \left[ \frac{W_{Li}}{D_L} + \frac{W_{Si}}{D_S} + V_U - V_T \right] \rho_i, \quad (6)$$



where

- $\rho_i$  = density of the ambient air at the time of the initial weighing, g/cm<sup>3</sup>,  
 $\rho_f$  = density of the ambient air at the time of the final weighing, g/cm<sup>3</sup>,  
 $V_T$  = external volume of the tare, cm<sup>3</sup>,  
 $V_U$  = external volume of the unknown U-tube, cm<sup>3</sup>,  
 $W_{Li}$  = calibrated value of weights 1 g and above at the time of the initial weighing, g,  
 $W_{Lf}$  = calibrated values of weights 1 g and above at the time of the final weighing, g,  
 $W_{Si}$  = calibrated value of weights less than 1 g at the time at the time of the initial weighing, g,  
 $W_{Sf}$  = calibrated values of weights less than 1 g at the time of the final weighing, g,  
 $D_L$  = density of weights 1 g and above, g/cm<sup>3</sup>, and  
 $D_S$  = density of weights less than 1 g, g/cm<sup>3</sup>.

Although  $C_b$  can be as large as 0.5 mg, it normally is of the order of 0.15 mg. Each of the terms in eq. (6) is summarized in the following subsections.

A-1-2-2-1 Air Density in the Balance Case (see [1] pp. 400-402). The density of the air in g/cm<sup>3</sup> is computed from the relation

$$\rho = \rho_o \times \frac{273.16}{T} \times \frac{(B - 0.003780 e_s \text{ RH})}{760}, \quad (7)$$

where  $T$  is the absolute temperature in K,  $B$  is the barometric pressure in Torr,  $e_s$  is the saturation vapor pressure of water at  $T$  in mm Hg at standard gravity and 0°C,  $\text{RH}$  is the relative humidity in percent at  $T$ , and  $\rho_o$  is the density of air at a pressure of 760 mm Hg and a temperature of 273.16K, and has a numerical value of  $1.29304 \times 10^{-3}$  g/cm<sup>3</sup> (A-1-4-1).

The standard deviation of the air density is  $0.32 \times 10^{-6}$  g/cm<sup>3</sup> and was computed at nominal values  $T = 298\text{K}$ ,  $B = 750$  mm Hg,  $\text{RH} = 40$  percent,  $e_s = 23.8$  Torr, and  $\rho = 1.167 \times 10^{-3}$  g/cm<sup>3</sup>. The steps are listed in table 1 together with the result.

A-1-2-2-2 External Volume of U-Tube (see [1] pp. 402-405). The external volume of each U-tube was determined by weighing in air and in distilled water. An equal-arm balance was mounted on a table, over an open cylinder of distilled water. A stainless steel wire was attached to the right pan and a 29.4-gram weight was suspended from the end of the wire and immersed in the water. A U-tube was then placed on the right pan and counter-balanced with weights on the left pan. This provided the U-tube weight in air. The U-tube was then attached to the wire, immersed in the cylinder of water, and again weighed. During these operations, the glass stopcocks were kept in the closed position. Precautions were taken to insure that the U-tube side arms were

filled with water and did not contain trapped air.

Consider the case where the U-tube is weighed in air. Let  $W_1$  be the weight suspended from the left pan and  $W_0$  the weight suspended from the right pan via the wire and immersed in the water. The weight  $W_1$  and the U-tube are buoyed up by displaced air of density  $\rho_1$  while the weight  $W_0$  is buoyed up by displaced water of density  $d_1$ . If the density of  $W_1$  is given by  $D$  and of  $W_0$  by  $D_0$ , and if the external U-tube volume at the ambient temperature is given by  $V_0$ , then it can be shown that

$$V_0 = \frac{W_1 - W_2}{(d_2 - \rho_1)} + \frac{W_2 (\rho_2/D) - W_1 (\rho_1/D)}{(d_2 - \rho_1)} - \frac{(W_0/D_0) (d_2 - d_1)}{(d_2 - \rho_1)} \quad (8)$$

where subscript 2 refers to the final conditions, i.e., the weighing operation with the U-tube suspended in water.

Nominal values  $W_1 = 98$  grams,  $W_2 = 33$  grams,  $W_0 = 29.4$  grams,  $d_1 = d_2 = 0.997$  g/cm<sup>3</sup>,  $D = 8.4$  g/cm<sup>3</sup>,  $D_0 = 11.3$  g/cm<sup>3</sup>,  $\rho_1 = \rho_2 = 0.00116$  g/cm<sup>3</sup>,  $d_2 - d_1 = 0.00025$  g/cm<sup>3</sup>, and the standard deviations for each independent variable yield  $0.017$  cm<sup>3</sup> as the computed standard deviation of the external volume  $s(V_0)$ . The computations and result are shown in table 2.

A-1-2-2-3 Error in the Buoyancy Correction (see [1] pp. 405-406). An estimate may now be made of the standard deviation of the buoyancy correction  $s(C_b)$ . For this computation, the following nominal values of the independent variables will be used:  $V_U - V_T = 10$  cm<sup>3</sup>,  $\rho_f = \rho_i = 0.00116$  g/cm<sup>3</sup>,  $W_{Lf} = W_{Li} = 10$  grams,  $D_L = 7.9$  g/cm<sup>3</sup>,  $D_S = 8.4$  g/cm<sup>3</sup>,  $\rho_f - \rho_i = 10^{-4}$  g/cm<sup>3</sup>, and  $W_{Sf} = W_{Si} = 0.5$  grams.

The calculations and the result are shown in table 3. The experimental standard deviation of the U-tube external volume,  $0.04$  cm<sup>3</sup>, is used in the calculations, since it is the larger of the calculated and experimental values. The standard deviation of the buoyancy correction is  $7.6 \times 10^{-6}$  gram.

A-1-2-3 Water Vapor Adsorption on External U-tube Surface (see [1] p. 406). Water vapor is adsorbed by metal and glass surfaces in proportion to the ambient relative humidity. Since the balance is symmetrical in its construction, the adsorption on the arms, pans and other components will tend to compensate and may therefore be neglected. The adsorption on the metal weights is also negligible in magnitude. At 50 percent RH and nominally room temperature, "Pyrex" is assumed to absorb  $0.11$   $\mu$ g/cm<sup>2</sup>, with a possible systematic error of  $\pm 0.11$   $\mu$ g/cm<sup>2</sup>. If the correction were ignored entirely, a maximum possible systematic error of  $\pm 0.2$   $\mu$ g/cm<sup>2</sup> would be introduced. Since the estimated maximum difference between external U-tube area and tare tube area is  $20$  cm<sup>2</sup>, and since the laboratory relative humidity is kept below 50 percent, it is seen that the correction may be ignored, leading to a maximum systematic error in U-tube weight of  $\pm 4$   $\mu$ g due to water vapor adsorption on

the external surfaces.

A-1-2-4 Static Charge on U-Tube. Static charge can accumulate on the pans of the balance and on the U-tube. The resultant force that is exerted on the arm of the balance will introduce an error. To avoid or reduce any accumulation of charge, several precautionary measures are observed. The metal balance case is grounded so that charge on the pan, or other metal parts, will tend to leak off. The glass panels and doors of the case are metalized. Strontium 90 is kept within the balance case, emitting beta rays which ionize the air in the immediate vicinity of the U-tube. In the presence of ionized air there is a greater tendency for any charge on the U-tube to leak off. Since static charge is evidenced by irregularities in the pointer swing, no reading is made until the swing is regular. There may still be residual static charge; the error this contributes, if any, cannot be readily estimated.

A-1-2-5 Handling. Whenever a U-tube is manipulated, as in opening or closing its stopcocks, or in inserting it in the drying train, a clean chamois skin or lens tissue is used to avoid bringing the fingers and hands of the operator into direct contact with the surfaces of the tube. After removal from the drying train, the side arms are cleaned with chamois skin or tissue to remove any residue from the "O" rings. The U-tube, when not in the drying train, or in the balance case, is kept in a covered plastic box to reduce any tendency for dust or dirt to accumulate on the external surfaces. It is dusted with a camel's hair brush prior to suspension from one arm of the balance. The tare is treated similarly. The magnitude of the error arising from handling is difficult to estimate and no attempt will be made to do so here, although it may be inferred from the experimental data subsequently presented (section A-1-2-10) that handling is one the largest factors contributing to the weighing error.

A-1-2-6 Mass of Internal Gas in U-Tube (see [1] p. 407). The internal volume of an empty U-tube is about 50 cm<sup>3</sup>. When filled with desiccant, the unoccupied volume is about 30 cm<sup>3</sup>. If air occupies this volume, then the weight of this air is part of the weight of the sealed U-tube. Not only can the temperature and pressure of the air at the time the U-tube is sealed differ for the initial and final weighings, but the internal unoccupied volume will decrease due to the absorption of water vapor by the desiccant. Unless a suitable correction is applied, an uncertainty in the difference between initial and final U-tube weights is thereby introduced. This correction may be as large as 1.6 mg.

The correction that must be applied to a differential U-tube weighing due to a changes in internal gas density and desiccant is

$$C_g = V_f \rho_f - V_i \rho_i = V_i (\rho_f - \rho_i) - v \rho_f, \quad (9)$$

where

$V_f$  = net internal U-tube volume at the time of the final weighing, cm<sup>3</sup>,  
 $V_i$  = net internal U-tube volume at the time of the initial weighing, cm<sup>3</sup>,  
 $\rho_f$  = density of the gas (usually air) in the U-tube at the time the U-tube is sealed in preparation for the final weighing, g/cm<sup>3</sup>,



$\rho_i$  = density of the gas (usually air) in the U-tube at the time the U-tube, is sealed in preparation for the initial weighing, g/cm<sup>3</sup>, and  
 $v$  = decrease in internal volume due to absorbed water, cm<sup>3</sup>.

A-1-2-6-1 Density of Gas in U-Tube. The density of the gas (taken here as dry air) sealed in the U-tube is computed from eq. (7) in which the relative humidity is zero. The standard deviation of the air density, estimated in a similar fashion to that described in A-1-2-2-1 is  $0.29 \times 10^{-6}$  g/cm<sup>3</sup>.

A-1-2-6-2 Initial Internal U-Tube Volume (see [1] pp. 407-408). To correct for the weight of air sealed in a U-tube, it is necessary to know the volume occupied by the air. If the U-tube is weighed separately with air and then with hydrogen, the initial internal volume can be computed using the equation

$$V_i = \frac{W_a - W_h}{\rho_a - \rho_h}, \quad (10)$$

where

$W_a$  = mass of U-tube filled with air, g,  
 $W_h$  = mass of U-tube filled with hydrogen, g,  
 $\rho_a$  = density of air in U-tube, g/cm<sup>3</sup>, and  
 $\rho_h$  = density of hydrogen in U-tube, g/cm<sup>3</sup>.

The standard deviation of the internal air density is  $0.29 \times 10^{-6}$  g/cm<sup>3</sup>. An analysis for the internal hydrogen density, the steps of which are shown in table 4, yields a standard deviation of  $2 \times 10^{-8}$  g/cm<sup>3</sup>.

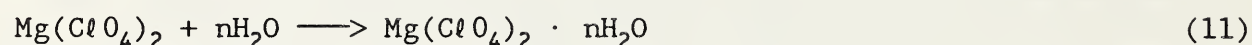
For the purpose of this computation, the experimentally-determined standard deviation of the mass change of a single U-tube based on flushing with dry gas, given in section A-1-2-10 will be used. Thus  $s(W_a) = s(W_h) = 0.08$  mg.

The standard deviation of the initial internal U-tube volume is  $s(V_i) = 0.11$  cm<sup>3</sup>, as shown in table 5.

A-1-2-6-3 Change in Internal U-Tube Volume. The internal volume of a U-tube is decreased between initial and final weighings because of the adsorbed water.

The first U-tube of the drying train absorbs on the order of 0.6 grams of water vapor. This tube contains magnesium perchlorate. When a gram-mole of  $Mg(ClO_4)_2$  absorbs water, the  $Mg(ClO_4)_2$  may combine with 2, 4 or 6 gram-moles of water [17] depending on the water available.

The reaction is





where  $n = 2, 4, \text{ or } 6$ .

Under the dynamic conditions existing in the case of a flow of moist gas through the desiccant, it is possible for the reaction to yield all three hydrate forms.

The internal volume decrease is given by

$$v = x(W_f - W_i) \quad , \quad (12)$$

where  $x$  is  $0.819 \text{ cm}^3/\text{g}$ ,  $W_f$  is the final U-tube weight in grams and  $W_i$  is the initial U-tube weight in grams. The magnitude of  $v$  is  $0.5 \text{ cm}^3$ . The value of  $0.819 \text{ cm}^3/\text{g}$  is obtained by assuming the true volume change per gram of water absorbed is midway between the value for the hexahydrate and that for the dihydrate.

The amount of water absorbed by the second and third tubes, which contain  $\text{P}_2\text{O}_5$ , is less than  $0.2 \text{ mg}$ . It can be shown that the volume change from the small amount of water absorbed is negligible [1].

A-1-2-6-4 Error in Internal Gas Mass. The random uncertainty in  $C_g$  may now be estimated. The details of the computations are given in table 6. Nominal values of  $30 \text{ cm}^3$  for  $V_f$  and  $V_i$  and of  $1.17 \times 10^{-3} \text{ g/cm}^3$  for  $\rho_f$  and  $\rho_i$  were used. The standard deviation  $s(C_g)$  so obtained is  $7.9 \times 10^{-5} \text{ gram}$ .

A-1-2-7 Incompleteness of Water Vapor Adsorption. Bower [18] has shown that the residual water vapor in a gas stream emerging for a U-tube filled with anhydrous  $\text{Mg}(\text{ClO}_4)_2$  is  $0.2 \times 10^{-2} \text{ mg/l}$  at a flow rate of 1 to 5 liter per hour, while Morley [19] has similarly demonstrated that an absorption tube packed with anhydrous  $\text{P}_2\text{O}_5$  will remove all but  $0.25 \times 10^{-4} \text{ mg}$  of water vapor per liter of air from a gas stream at a flow rate of three liters per hour. The flow rate used in the gravimetric hygrometer may be as large as 2 liter per minute. Because of the large difference in flow between Morley's work and the present work, no correction will be made, and the systematic error in the weight of water arising from the incompleteness of absorption will be conservatively assigned a maximum value of  $0.5 \times 10^{-4} \text{ mg/l}$  of air collected.

A-1-2-8 Random Errors in the Measurement of Mass of Water Vapor. A numerical estimate will now be made for the random error involved in the measurement of the mass of water collected in a U-tube based on the uncertainties of the various independent parameters discussed above. The standard deviation  $s(m)$  is given by eq. (5). The individual sources of random error, the magnitudes of their contributions, and the computed standard deviation  $s(m)$  are summarized in table 7.

The standard deviation of the mass change of the first tube is  $81 \times 10^{-6} \text{ gram}$ , and of the second and third tubes is  $25 \times 10^{-6} \text{ gram}$ . The figures represent the error in mass gain in a tube where both the initial and final masses are each based on a single weighing.

A-1-2-9 Systemic Errors in the Mass of Water Vapor. There are two non-

negligible systematic errors which must be considered. The first, arising from the differences in surface area of the U-tube and tare and the water vapor absorbed on these surfaces, was discussed in A-1-2-2-4 and A-1-2-3. The maximum error expected from this effect was  $\pm 4 \mu\text{g}$  per tube, and since two tubes are used for the water vapor mass determination, the maximum error for the water vapor mass determination is  $\pm 8 \mu\text{g}$ .

The other systematic error was discussed in A-1-2-6-3. The maximum uncertainty in the constant  $x$  of eq. (12), important only for the first tube in the drying train, was  $\pm 0.057 \text{ cm}^3/\text{g}$ . Assuming that 0.6 g of water is absorbed in this first tube, it is seen that a maximum uncertainty of  $\pm 0.034 \text{ cm}^3$  arises in the internal volume. Since the nominal air density in the tube is  $1.17 \text{ mg}/\text{cm}^3$ , the systematic error in the mass of internal air and hence in the mass of water vapor collected may be as much as  $\pm 0.04 \text{ mg}$ .

The total possible systematic error in the mass of water vapor is therefore  $0.04 + 0.008 = \pm 0.048 \text{ mg}$ .

A-1-2-10 Blank Runs. Two types of experiments were performed to provide a check on the computed estimate of the error in the determination of the mass of water vapor absorbed by the main drying train. These experiments traced the degradation in accuracy of the weighing process with increasing complexity of the handling and manipulating operations.

The first experiment consisted of blank runs in which the actual conditions of a mixing ratio determination were simulated, except that air which had been successively predried by  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{P}_2\text{O}_5$  passed through the U-tubes. Each desiccant-filled U-tube in this experiment was weighed, removed from the balance, stored, and subsequently inserted into the main drying train along with one or two other filled U-tubes. Its stopcocks were opened, it was flushed with the predried air at a flow rate of about 1.7 lpm, its stopcocks were closed, and it was reweighed.

The tube was weighed at least twice (generally three times or more) prior to a run, from which an average initial weight was computed. An identical procedure yielded an average final weight. The average final weight of one run was used as the initial average weight of the following run. Since the change in mass should be zero, the difference between the initial and final weight is a measure of the error. Three different U-tubes were used to form a total of fifteen runs. The results are shown in table 8.

The losses and gains in weight (differences) are almost equal in number and the sum of these is essentially zero. The blank runs did not disclose any systematic error. After applying a method for pooling data described by Youden [12], and assuming that these results may be extrapolated to actual mixing ratio determinations, it is estimated that the gain in mass in a single U-tube can be measured with a standard deviation of 0.080 mg and in two tubes, 0.113 mg.

A second experiment was performed in which a given mass of water was added to a stream of pre-dried air and was subsequently removed by the drying train. The water source was a U-tube containing about 1 gram of distilled

water through which the air passes at a rate of flow of approximately 1.5 lpm. The mass of water lost by the source was compared to the gain in mass by the first two tubes in the drying train. The third tube, in accordance with the practice adopted in this work, was used only as a guard tube.

Each of the U-tubes, the one containing water, and the three in the drying train containing desiccant were weighed from two to five times before and after a run to provide average values for the initial and final weights.

Five runs were made. The results are given in table 9. The differences between the mass increase in the drying train and the mass decrease in the water source show roughly equal numbers of plus and minus signs, indicating no pronounced tendency that could be ascribed to systematic effects. As in the previous experiment, the differences will be assumed due to random errors. The standard deviation of a single determination of the difference between the water available and that gained is 0.16 mg. This is consistent with the results of the dry gas experiment which yielded 0.080 mg as the standard deviation for the mass determination of a single U-tube. Since three tubes were involved in each of the present runs (one tube with water and two tubes with desiccant), the predicted standard deviation of a run, based on 0.080 mg is  $\sqrt{3} \times 0.080$  mg or 0.14 mg. Inversely, it could be stated that the final experiment yields a standard deviation of 0.092 mg for the mass determination by a single U-tube in the main drying train so that the standard deviation of the sum of the water vapor mass determinations by the first and second tubes is  $\sqrt{2}(0.092) = 0.13$  mg. The standard deviation of the water vapor mass determination for any run therefore will be assumed to be 0.13 mg.

#### A-1-3 MEASUREMENT OF THE GAS VOLUME (see [1] pp.413-418)

The internal volumes of the two cylinders were measured by weighing each cylinder empty and then filled with distilled water. Each cylinder volume was computed using the equation

$$V_c = \frac{M}{d} - C_v \quad (13)$$

where

- M = mass of water required to fill the cylinder at temperature  $t_c$ , grams,
- d = density of water at temperature  $t_c$  and pressure B, g/cm<sup>3</sup>,
- $V_c$  = volume at temperature  $t_c$  and pressure B, cm<sup>3</sup>, and
- $C_v$  = correction for water trapped in cylinder valves during filling operation, cm<sup>3</sup>.

Five independent determinations were made of each cylinder volume. Since the ambient conditions were not controlled, each determination involved a different temperature and barometric pressure. At atmospheric pressure, the change in cylinder volume due to barometric fluctuations is negligible; the change because of temperature fluctuations, on the other hand, is significant. Each experimental value of cylinder volume was therefore adjusted to the



volume it would have at 25°C, and these adjusted volumes were averaged to give a mean value.

Thus

$$V_o = V_c + C_x , \quad (14)$$

where

$V_o$  = volume at 25°C and atmospheric pressure,  $\text{cm}^3$ , and  
 $C_x$  = correction for adjusting each experimentally determined volume to that of 25°C.

The mean cylinder volume is

$$\bar{V}_o = \frac{\Sigma V_o}{n} , \quad (15)$$

where

$\Sigma V_o$  = sum of the experimentally determined and adjusted volumes,  $\text{cm}^3$ ,

and

$n$  = number of experimental determinations.

The calibration results are given in table 10. Each cylinder has a volume capacity of about 29.7 liters at 25°C.

In an actual run in which a moisture determination is being made, the cylinders may not be at the standard temperature of 25°C. It will be necessary to adjust the mean cylinder volume to that of the test temperature by applying a correction whose magnitude will depend on the difference between these two temperatures, thus

$$V = \bar{V}_o + C_t \quad (16)$$

where

$V$  = volume of the cylinder test temperature,  $\text{cm}^3$ , and  
 $C_t$  = correction for adjusting the mean cylinder volume to that at the test temperature,  $\text{cm}^3$ .

An analysis will now be made to obtain an estimate of the uncertainty in  $\bar{V}_o$  based on all known sources of error and this uncertainty will then be compared with the uncertainties derived from the experimental volume determinations shown in table 10. Finally, the uncertainty in determining  $V$  will be estimated.

A-1-3-1 Mass of Water. The mass of water required to fill a cylinder was determined by weighing the cylinder empty and then full using the substitution weighing method on a 50 kg balance. The accuracy of this mass determination



is influenced by the variability of the balance, the calibration of the weights, and the correction for buoyancy of the cylinder and the weights. The mass of water was computed using the equation

$$M = W_f - W_i + C_w + C_b + C_r, \quad (17)$$

where

- $M$  = mass of water, grams,
- $W_f$  = sum of face values of the weights used to balance the filled cylinder, grams,
- $W_i$  = sum of face values of the weights used to balance the empty open cylinder, grams,
- $C_w$  = sum of the corrections applied to the face values of the weight, grams
- $C_b$  = buoyancy correction, grams, and
- $C_r$  = correction for the inequality of balance arm lengths, grams.

A-1-3-1-1 Balance and Weights. The variability of the 50 kg balance was assessed from the reciprocal sensitivity, with a given weight on both pans, and from the reproducibility of the rest point for that weight. With nominal loads on the pans of 30.5 kg and 60.1 kg, corresponding to the initial and final weights of a cylinder, the largest reciprocal sensitivities observed were 76 mg/division and 112 mg/division, and the greatest uncertainties in the rest point reproducibilities were 0.6 division and 0.8 division, respectively. Therefore, the maximum uncertainty arising from the nonreproducibility of the balance was 46 mg in  $W_i$  and 90 mg in  $W_f$ , so that the standard deviations were 15 mg and 30 mg, respectively.

The balance arm length ratio as experimentally determined by transposition weighing differs from unity by 2.5 ppm. This introduced a systematic error in the differential cylinder weight of  $(W_f - W_i) \times 2.5 \times 10^{-6}$  gram or 74 mg. A corresponding correction was applied, and the residual uncertainty was probably no greater than 1/2 ppm or 15 mg so that the standard deviation of  $C_r$  was 5 mg. The 1/2 ppm uncertainty contributes maximum errors of 30 mg and 15 mg in  $W_f$  and  $W_i$ , respectively.

The value for  $C_w$  was computed from the calibration corrections supplied by the NBS Length and Mass Division for the specific set of Class S weights [3] used, which, for weights of 10 grams and above were determined with a maximum uncertainty of 3 ppm. Since  $W_f - W_i$  was 29.6 kg, it follows that the maximum uncertainty in  $C_w$  was 89 mg and the standard deviation of  $C_w$  was 30 mg. Furthermore, the 3 ppm uncertainty contributes maximum uncertainties in the corrected values of  $W_f$  and  $W_i$  alone of 180 mg and 90 mg, respectively.

A-1-3-1-2 Buoyancy Correction. It can be shown that the buoyancy correction,  $C_b$ , is given by

$$C_b = (W_f - W_i) \frac{\rho_f}{\rho_{H_2O}} - W_f \frac{\rho_f}{\rho_w} + W_i \left[ \frac{\rho_f}{\rho_x} + \frac{\rho_i}{\rho_w} - \frac{\rho_i}{\rho_x} \right] \quad (18)$$

where

- $W_f$  = sum of corrected values of the weights used to achieve equilibrium with the filled cylinder, grams,
- $W_i$  = sum of corrected values of the weights used to achieve equilibrium with the empty open cylinder, grams,
- $\rho_i$  = density of the air at the time of the weighing of the empty cylinder, g/cm<sup>3</sup>,
- $\rho_x$  = density of the open and empty cylinder, g/cm<sup>3</sup>, and
- $\rho_w$  = density of the weights, g/cm<sup>3</sup>.
- $\rho_f$  = density of the air at the time of the weighing of the filled cylinder, g/cm<sup>3</sup>, and
- $\rho_{H_2O}$  = density of the water in the cylinder, g/cm<sup>3</sup>.

The magnitude of  $C_b$  is about 31 grams. Consider now the errors involved in computing  $C_b$ .

The air density was calculated using eq.(7). The estimate of uncertainty in the air density is  $s(\rho_i) = s(\rho_f) = 0.42 \times 10^{-6}$  g/cm<sup>3</sup>.

The estimate of the uncertainty in the water density is  $s(\rho_{H_2O}) = 45 \times 10^{-6}$  g/cm<sup>3</sup>. The error in the assumed density of the weights may be as large as  $\pm 0.1$  g/cm<sup>3</sup>, giving rise to a systematic error in  $C_b$  of  $\pm 0.06$  gram.

The cylinders and the attached valves were fabricated from stainless steel which has a nominal density of 7.8 g/cm<sup>3</sup>. However, attached to the cylinders were a few small brass fittings used in the filling operation and coupled to the valves were aluminum air actuators. The uncertainty in the nominal density is systematic and may be as great as  $\pm 0.2$  g/cm<sup>3</sup> leading to a maximum contribution to the buoyancy error of  $\pm 0.001$  gram.

The maximum uncertainties for  $W_i$  due to the balance variability, the calibration error, and the inequality of arms, were 46, 90 and 15 mg for a total of 151 mg; for  $W_f$  the corresponding contributions were 90, 180 and 30 mg for a total of 300 mg. The standard deviations will be assumed to be  $s(W_i) = 50$  mg and  $s(W_f) = 100$  mg.

The following nominal values were utilized in calculating the numerical values of the partial derivatives.  $W_i = 30.55$  kg,  $W_f = 60.13$  kg,  $\rho_i = \rho_f = 1.161 \times 10^{-3}$  g/cm<sup>3</sup>,  $\rho_{H_2O} = 0.997$  g/cm<sup>3</sup>,  $\rho_w = 8.4$  g/cm<sup>3</sup>,  $\rho_x = 7.8$  g/cm<sup>3</sup>,  $\rho_f - \rho_i = 10^{-5}$  g/cm<sup>3</sup>.

The steps in the computation of the uncertainty in  $C_b$  due to random effects are given in table 11. The estimate for the standard deviation  $s(C_b)$  is 0.113 gram.

A-1-3-1-3 Error in Mass Determination. The random uncertainty in the mass determination is computed from the equation

$$s(M) = [s^2(W_f) + s^2(W_i) + s^2(C_w) + s^2(C_r) + s^2(C_b)]^{1/2} . \quad (19)$$

Note that in this case,  $W_f$  and  $W_i$  are the uncorrected values [as opposed to the case in eq. (18)], and their errors depend only on the balance variability and arm ratio errors. The maximum errors from these sources are 120 mg in  $W_f$  and 61 mg in  $W_i$ , leading to the respective standard deviations of 40 mg and 20 mg.

The calculations in table 12 show that  $s(M) = 0.125$  g.

A-1-3-2 Water Density. The sources of error in the density of the water used in the cylinder volume determination are the same as those discussed in A-1-3-1. The same value for the standard deviation of the density estimated there will be used here, that is,  $45 \times 10^{-6}$  g/cm<sup>3</sup>.

A-1-3-3 Cylinder Valve Correction. The cylinder volume is that volume enclosed by the shut inlet valve, barometer valve, and vacuum gage valve. In filling the cylinder with water for calibration, a procedure was followed whereby water was unavoidably or inadvertently trapped in one or more of the valves. This trapped water, which filled the channel in the ball of the valve was, of course, weighed. A volumetric correction, based on the geometry of the channel, was therefore made to reduce this systematic error. This correction was computed by the equation

$$C_v = \frac{\pi D^2}{4} \times L_c , \quad (20)$$

where  $D$  is the diameter of the cylindrical channel and  $L_c$  is the length of the channel. Since  $D$  is 3/8-in and  $L_c = 3/4$ -in for the 1/4-in valve (water was not trapped in the large valve),  $C_v$  is 1.36 cm<sup>3</sup>.

The maximum uncertainty  $\Delta C_v$  is estimated from the equation

$$\Delta C_v = \frac{\partial C_v}{\partial D} \Delta D + \frac{\partial C_v}{\partial L_c} \Delta L_c , \quad (21)$$



where

$$\frac{\partial C_v}{\partial D} = \frac{\pi D L_c}{2} , \quad (22)$$

$$\frac{\partial C_v}{\partial L_c} = \frac{\pi D^2}{4} , \quad (23)$$

$\Delta D$  = maximum uncertainty in  $D$ , and

$\Delta L_c$  = maximum uncertainty in  $L_c$ .

At the time this work was done, normal engineering tolerances permitted a maximum error of  $\pm 1/64$ -inch in any dimension. In the absence of any direct measurements of  $D$  or  $L_c$ , it will be assumed that the maximum uncertainty in each is  $\pm 1/64$ -in from which it follows that  $\Delta C_v$  for a single valve is  $\pm 0.14$   $\text{cm}^3$  and for three valves,  $\pm 0.42$   $\text{cm}^3$ . This error is systematic. The standard deviation  $s(V_c)$  as indicated in table 13, is  $1.34$   $\text{cm}^3$ .

A-1-3-4 Correction to a Standard Temperature. The following correction was applied to each experimentally determined cylinder volume in order to adjust it to the value it would have at the standard temperature of  $25^\circ\text{C}$ :

$$C_x = V_c \alpha (t_o - t_e) , \quad (24)$$

where

$$\begin{aligned} C_x &= \text{correction, cm}^3, \\ \alpha &= \text{coefficient of volumetric expansion for the cylinder,} \\ &\quad \text{cm}^3/(\text{cm}^3 \cdot ^\circ\text{C}), \\ t_o &= \text{standard temperature, i.e., } 25^\circ\text{C}, \\ t_e &= \text{temperature at which volume } V \text{ was determined, } ^\circ\text{C}, \text{ and} \\ V_c &= \text{volume of cylinder at temperature } t_e, \text{ cm}^3. \end{aligned}$$

The cylinder was fabricated from type 316 stainless steel.

Interpretations of the data of Furman [20], Beenaker and Swenson [21], Lucks and Deem [22], and the Metals Handbook [23] lead to values of the coefficient of linear expansion of 316 stainless steel of 15.2, 15.6, 15.3, and 15.8, all in units of  $10^{-6}$   $\text{cm}/(\text{cm} \cdot ^\circ\text{C})$ . If all these values are given equal weight, the mean is  $15.48 \times 10^{-6}$   $\text{cm}/\text{cm}/^\circ\text{C}$ . Assuming that the coefficient of volumetric expansion is three times the coefficient of linear expansion, then the mean  $\alpha = 46.4 \times 10^{-6}$   $\text{cm}^3/(\text{cm}^3 \cdot ^\circ\text{C})$  with a standard deviation of the mean of  $0.45 \times 10^{-6}$   $\text{cm}^3/(\text{cm}^3 \cdot ^\circ\text{C})$ . The correction per  $^\circ\text{C}$ , that is,  $C_x/(t_o - t_e)$ , is  $29700$   $\text{cm}^3 \times 46.4 \times 10^{-6}$   $\text{cm}^3/(\text{cm}^3 \cdot ^\circ\text{C})$  or  $1.38$   $\text{cm}^3/^\circ\text{C}$  where  $29700$   $\text{cm}^3$  is the nominal cylinder volume.



The following nominal values of the parameters were used in the calculation:

$$\begin{aligned}\alpha &= 46.4 \times 10^{-6} \text{ cm}^3/(\text{cm}^3 \cdot ^\circ\text{C}), \\ V_c &= 29700 \text{ cm}^3, \text{ and} \\ (t_o - t_c) &= 2^\circ\text{C}.\end{aligned}$$

The computations and results are shown in table 14. The standard deviation  $s(C_x)$  is  $0.14 \text{ cm}^3$ .

A-1-3-5 Random Error in the Measurement of Gas Volume. The estimated standard deviation of the volume adjusted to  $25^\circ\text{C}$ ,  $s(V_o)$ , is given by  $[s^2(V_c) + s^2(C_x)]^{1/2}$  or  $1.35 \text{ cm}^3$ . The estimated standard deviation of the mean volume  $s(V_o)$ , based on  $n$  repeated determinations of  $V_o$ , is  $s(V_o)/\sqrt{n}$  which reduces to  $0.60 \text{ cm}^3$  for  $n = 5$ . The experimental standard deviations of the mean volume determinations were  $2.15 \text{ cm}^3$  and  $0.99 \text{ cm}^3$  for cylinder Nos. 1 and 2 respectively (table 10). It is apparent that the estimate of the uncertainty in the volume determination based on an error analysis yields a value that is of the same order of magnitude as the experimental uncertainty.

If the gas volume measuring system, during a moisture determination, is maintained at some temperature other than  $25^\circ\text{C}$ , then the mean volumes, listed in table 10, must be adjusted to the test temperature  $t$  by adding

$$C_t = \bar{V}_o \alpha (t - 25^\circ\text{C}) , \quad (25)$$

as indicated in eq. (15).

It follows that for each degree difference between  $t$  and  $t_o$ , the standard deviation of  $C_t$  is  $0.02 \text{ cm}^3$  and therefore,

$$s(V) = [s^2(\bar{V}_o) + 0.0004(t - 25^\circ)^2]^{1/2} . \quad (26)$$

A-1-3-6 Systematic Errors in the Gas Volume. The non-negligible systematic errors in the cylinder volumes and thus in the gas volumes arise in the buoyancy correction (A-1-3-1-2) and the cylinder valve correction (A-1-3-3). The former leads to a maximum uncertainty in  $C_b$  and thus in the water mass of  $\pm 0.061 \text{ gram}$ . This corresponds to a maximum uncertainty in the cylinder volume of  $\pm 0.06 \text{ cm}^3$ . The latter leads to a maximum uncertainty in the cylinder volume of  $\pm 0.42 \text{ cm}^3$ . Altogether there is a maximum possible systematic error in the cylinder volume of  $\pm 0.48 \text{ cm}^3$ .

#### A-1-4 DETERMINATION OF THE GAS DENSITY IN A CYLINDER (see [1] pp.418-423)

The gas of principal interest in humidity measurement is atmospheric air; hence, the discussion and error analysis will be confined to this gas although similar analyses may be made for other gases.

A-1-4-1 Standard Density. Air is a mixture of oxygen, nitrogen, argon and carbon dioxide. The percentage composition of the components is essentially constant. Such variables as geographic location, altitude, and presence of sources of contamination have little detectable effect on the percentage composition [24]. The percentages by volume as given by Harrison [25] are as follows: Nitrogen, 78.084; Oxygen, 20.948; Carbon Dioxide, 0.0314 and Argon, 0.934. These values are based generally on the average of results of chemical analyses made at various times and places [25].

The value of  $\rho_o$ , the density of air at 273.16K and 760 mm Hg, is computed from the equation

$$\rho_o = \frac{M_a}{V_a} = \frac{M_a}{Z_o V} \quad , \quad (27)$$

where  $M_a$  is the molecular weight of air in g/mole, and  $V_a$  is the molar volume in  $\text{cm}^3/\text{mole}$  that air occupies under standard conditions. Since air is not an ideal gas,  $V_a$  is equal to  $V$ , the molar volume an ideal gas occupies under standard conditions, multiplied by  $Z_o$ , the compressibility factor for air at 273.16K and 760 Torr.

The molecular weight of air is given by

$$M_a = \%N_2(M_{N_2}) + \%O_2(M_{O_2}) + \%CO_2(M_{CO_2}) + \%A(M_A) \quad , \quad (28)$$

where the M's and their corresponding subscripts denote the molecular weights of the four components listed above.

Therefore  $\rho_o$  is given by

$$\rho_o = [ \%N_2(M_{N_2}) + \%O_2(M_{O_2}) + \%CO_2(M_{CO_2}) + \%A(M_A) ] / VZ_o \quad . \quad (29)$$

Using the above percentages for the components and the following value for their molecular weights,  $N_2 = 28.016$  g/mole,  $O_2 = 32$  g/mole,  $CO_2 = 44.011$  g/mole, and  $A = 39.944$  g/mole, and using  $V = 22414.6 \text{ cm}^3$  [26], and  $Z_o = 0.99941$ [4], it is found that  $\rho_o = 1.29304 \times 10^{-3} \text{ g/cm}^3$ .

The fact that there are uncertainties in  $\rho$  arising from uncertainties in composition will be taken into account by assuming these uncertainties contribute to the standard deviation of  $\rho_o$ .

According to information available at the National Institute of Standards and Technology (formerly National Bureau of Standards) [27], the contribution of maximum uncertainties in the molecular weights of the constituents to the maximum uncertainty of the molecular weight of air is 4 or

5 parts in  $10^5$  from nitrogen, and a maximum of 1 part in  $10^5$  for the remaining components. This gives a total maximum uncertainty of 6 parts per  $10^5$ . Applying the 3 sigma rule, the standard deviation of the molecular weight of air is 2 parts in  $10^5$ . The molecular weight of air is 28.966 g/mole as computed from eq. (28). Therefore its standard deviation, arising from uncertainties in the molecular weights of the components, is  $6 \times 10^{-4}$  g/mole.

The standard deviation of  $V$  is  $0.9 \text{ cm}^3$  [26].

According to Hilsenrath [4], the uncertainty in  $Z_0$  is nominally zero.

From the computations in table 15, the standard deviation of  $\rho_0$  is  $0.1 \times 10^{-6} \text{ g/cm}^3$ .

The density of air at any other temperature and pressure is given by

$$\rho = \rho_0 \times \frac{273.15}{T} \times \frac{B}{760} \times \frac{Z_0}{Z}, \quad (30)$$

where  $Z$ , the compressibility factor, is a function of  $T$  and  $B$ .

Hilsenrath [4] has shown that the differences between compressibility factors of his tables and the tables obtained by other researchers, at a nominal pressure of 1 atm, is zero at 273.16K and 1 part in  $10^4$  at 323.15K. If this is interpolated linearly, the difference increases 2 parts in  $10^6$ /K. Therefore at 300K, the difference is 5.4 parts in  $10^5$ . This will be taken as the standard deviation of the compressibility factor for the present purpose.

The compressibility factor at one atmosphere and 300K is nominally unity, so its standard deviation is  $54 \times 10^{-6}$ .

A-1-4-2 Pressure. The accuracy with which the pressure in a cylinder can be measured depends on the barometer errors, the residual gas pressure at the cessation of evacuation, the fluctuations at the assumed equilibrium point, leakage in the barometer system and the error due to the difference between the pressure in the barometer system and that in the cylinder at the moment the barometer valve is opened.

A precision micrometer cistern mercury barometer is used to measure the equilibrium pressure within a cylinder. This instrument was calibrated by the NES Pressure and Vacuum Section in the latter part of 1960. After applying corrections for the zero reading, capillary depression, temperature, and gravity, it is estimated that the standard deviation of a pressure measurement, arising from the barometer itself, is 0.08 Torr.

The barometer scale was independently calibrated with gage blocks, with another mercury manometer, and with a piston gage. At  $10^\circ\text{C}$  and 700 Torr, the gage block calibration indicates a scale correction of -0.005 Torr, whereas both of the other methods indicate nominal scale corrections of +0.120 Torr.



Because of this discrepancy, a correction of +0.065 Torr will be applied to any reading, and a residual systematic error of  $\pm 0.075$  Torr will be assigned to any reading.

The equilibrium values of the pressures in a given cylinder with repeated evacuation and filling have varied as much as 1.3 Torr, although a more typical value would be 0.5 Torr. The variations arise from the photocell circuit response time and the variability of the flow rate at this part of the cycle. Because of the magnitude of the variations, the actual pressure must be recorded each time equilibrium has been reached.

Fluctuations also occur after the cylinder has presumably attained equilibrium. Since it is not known whether these fluctuations arise from the nonreproducibility of the barometer or are real fluctuations, the latter will be assumed, in which case this contributes another uncertainty to the pressure. The largest such fluctuation has been about 0.2 Torr, although the more usual figure is 0.025 Torr. The standard deviation will be assumed to be represented by 1/3 of the maximum, that is, 0.07 Torr.

The total standard deviation of a single pressure reading, because of errors in the barometer itself and the fluctuations which occur is given by

$$s(p) = [(0.08)^2 + (0.07)^2]^{1/2} , \quad (31)$$

or  $s(p) = 0.10$  Torr.

At least three barometer readings are taken after the cylinder has reached its equilibrium pressure, and these are averaged. The standard deviation of the average pressure within a cylinder is thus given by

$$\frac{s(p)}{\sqrt{3}} = 0.06 \text{ Torr.} \quad (32)$$

The barometer system (i.e., the cistern and connecting tubing) is not necessarily at the equilibrium pressure of the cylinders before a run is started. As a result, air from the system is dumped into a cylinder, or vice versa (depending on which is initially greater), resulting in a pressure reading that depends both on the true cylinder pressure and on the pressure in the barometer system before connection to the cylinder. The excess air is shunted back and forth between cylinders as they open and close, so that the correction need only be applied once, upon completion of the run.

The correction is of the form

$$P_c = \frac{V_s \Delta P + A(P_f^2 - P_i^2)}{V_c} \quad (33)$$



where

$V_s$  = barometer system volume when column and cistern are at same pressure,  $\text{cm}^3$ ,  
 $P_f$  = final cylinder pressure reading on barometer, cm,  
 $P_i$  = initial pressure reading on barometer before run begins, cm,  
 $\Delta P$  =  $P_f - P_i$ , cm,  
 $A$  = area of barometer column,  $\text{cm}^2$ , and  
 $V_c$  = volume of cylinder to which the barometer is finally connected,  $\text{cm}^3$ .

The same correction applies for the pressure switch, although for it  $P_f$  and  $P_i$  represent final and initial ambient pressures. The sum of the two corrections is about 0.1 Torr.

The residual errors, after applying the correction to both systems, are estimated to be one part in 40,000 if the pressure reading is 100 Torr or greater, that is, when a cylinder has collected 1/7 of its volume, or nominally 4.2 liters.

The leak rate of the barometer system is such that the mercury column moves 0.006 mm/min (essentially equivalent to .006 Torr/min) under a vacuum of less than 100 millitorr.

The length of time the barometer system is open to a cylinder is roughly 10 minutes, the latter half of which is under equilibrium conditions. If the leak rate was 0.006 Torr/min at the equilibrium pressure of 695 Torr, the column would be expected to move upward 0.03 Torr during the reading time. This is not observed, indicating that error from the leak rate at the equilibrium pressure is negligible.

Each cylinder was repeatedly evacuated to determine its residual pressure just prior to filling. These tests showed that each cylinder reached 50 millitorr in about 93 seconds.

At the time of the momentary closing and reopening of the vacuum valve of the cylinder being evacuated, i.e., 120 seconds after the start of evacuation, the cylinder pressure was about 37 millitorr. The closing and reopening of the valve is a deliberate action to remove gas trapped in the valve channel. It causes the cylinder pressure to rise again to approximately 75 millitorr after which it returns to the value it had prior to the closing in approximately 90 seconds.

At the maximum flow rate of 2 lpm of air into one cylinder, the other cylinder was evacuated for about 420 seconds, at which time the pressure in that cylinder was reduced to about 23 millitorr.

Both cylinders had residual pressures of less than 20 millitorr after evacuation for 600 seconds, and after 2100 seconds the pressures had decreased to 17 millitorr.

The residual back pressure within the cylinder when it is opened for filling after evacuation, as measured with the system's thermocouple vacuum gage, is no greater than 20 millitorr. This is a systematic error for which a correction may be applied. However, the magnitude of this error, about 1 part in 35,000, is so small that it may be neglected. The scatter of the observations after repeated evacuations is about 10 millitorr, which is only 1 part in 70,000 of the equilibrium pressure of 695 Torr and thus negligible. Therefore, the only random factor contributing to the accuracy of the cylinder pressure that is significant is the barometer error which is 0.06 Torr.

A-1-4-3 Temperature. The uncertainties in the temperature measurement of the gas in the cylinder arise from the error in the thermopile calibration, the accuracy of the potentiometer used for measuring the thermopile voltage, and the fluctuations about the mean equilibrium temperature.

Each thermopile was calibrated at nominal temperatures of 20, 25, 30 and 35°C against a NBS calibrated platinum resistance thermometer for which the estimated maximum error is 0.001°C. The thermopile has an output of about 160  $\mu\text{V}/^\circ\text{C}$ ; the potentiometer used to measure this output has a maximum uncertainty of 1  $\mu\text{V}$ ; therefore, the calibration data had an equivalent maximum uncertainty of 0.006°C. In order to permit interpolation between thermopile calibration points, the data were fitted to an empirical equation of the form

$$E = at + bt^2 + ct^3 + dt^4 . \quad (34)$$

This equation was used to compute the EMF outputs for temperatures at 0.5°C intervals, and straight lines were then drawn between successive points. These lines are used to convert EMF readings into temperature. A comparison of interpolated values, as derived from the curves and the experimental data disclosed that the maximum difference was 0.011°C. Subsequent to the calibration, each measurement with the thermopile involves the use of the potentiometer so that the latter again contributes an uncertainty of 0.006°C.

The equilibrium temperature fluctuated about 0.002°C. Since it is not known whether this is because of the nonreproducibility of the thermopiles or whether it is real, an error of this magnitude will be assigned to the temperature.

The sum of the uncertainties in the measurement of cylinder temperature is thus 0.026°C. It will be assumed, therefore, that the standard deviation of the gas temperature in the cylinder at equilibrium is 0.009 deg C, that is, 1/3 of the maximum uncertainty.

A-1-4-4 Random Error in the Determination of Gas Density. Using the appropriate partial derivatives of eq. (29), along with the required standard deviations, leads to the terms contributing to the uncertainty in the gas density. The nominal values used for the independent parameters are  $\rho_0 = 1.3 \times 10^{-3} \text{ g/cm}^3$ ,  $Z_0/Z = 1$ ,  $T = 298\text{K}$ , and  $B = 700 \text{ Torr}$ . As indicated in table 16,  $s(\rho) = 0.14 \times 10^{-6} \text{ g/cm}^3$ . These values vary slightly with temperature, but the variations are insignificant for the present purpose.

A-1-4-5 Systematic Error in the Determination of Gas Density. The only

non-negligible systematic error occurring in this determination is that arising from the uncertainty of the scale correction to the barometer. As mentioned in A-1-4-2, the magnitude of this error is  $\pm 0.075$  Torr.

Use of the density equation [eq. (7)] shows that the magnitude of the corresponding systematic error in the air density is  $\pm 0.12 \times 10^{-6}$  g/cm<sup>3</sup>.

## A-2 ANALYSIS OF COMPLETE SYSTEM

### A-2-1 ACCURACY IN THE DETERMINATION OF MIXING RATIO (see [1] pp.423-428)

A-2-1-1 Random Error in the Mixing Ratio. The mixing ratio is defined by eq. (1) while the standard deviation of the mixing ratio is given by eq. (2). The latter equation is repeated here.

$$s(r) = [(\frac{\partial r}{\partial M})^2 s^2(M) + (\frac{\partial r}{\partial V})^2 s^2(V) + (\frac{\partial r}{\partial \rho})^2 s^2(\rho)]^{1/2} , \quad (35)$$

where

$$\frac{\partial r}{\partial M} = \frac{1}{V\rho} , \quad (36)$$

$$\frac{\partial r}{\partial V} = - \frac{M}{V^2\rho} , \text{ and} \quad (37)$$

$$\frac{\partial r}{\partial \rho} = - \frac{M}{V\rho^2} . \quad (38)$$

It will be convenient to use relative errors rather than absolute errors at this time. If both sides of eq. (35) are divided by the mixing ratio  $r$ , then

$$\frac{s(r)}{r} = [ \frac{s^2(M)}{M^2} + \frac{s^2(V)}{V^2} + \frac{s^2(\rho)}{\rho^2} ]^{1/2} . \quad (39)$$



The nominal value of M is dependent on the duration of a test run, the flow rate of the test gas, and the moisture content of the test gas, whereas  $s(M)$  is essentially independent of these parameters. If the test gas has a high moisture content, then at the design flow rates of this apparatus, in a relatively short time enough moisture can be collected in the drying train so that the relative errors  $s(M)/M$  is reasonably small. However, as the moisture content of the test gas decreases, to collect the same mass of water the duration of a run must be increased. At a given flow rate a low enough moisture content will eventually be reached for which the duration of a run will be inordinately long to maintain the same relative error. Thus for moisture contents below this value, the duration of the run will be the factor limiting the accuracy.

It has been estimated that M can be determined with a standard deviation of  $13 \times 10^{-5}$  grams provided all the moisture is removed by the first two U-tubes in the main drying train. Assuming that 0.6 gram of water are collected, the relative error is thus  $13 \times 10^{-5} / 0.6$  or 2.2 parts in  $10^4$ .

The volume of the test gas will be the sum of the number of times each cylinder is filled multiplied by its calibrated volume. The error is the same for each cylinder, so that the total error is the number of fillings times the error for a single filling. Hence the relative error in the total dry air volume is

$$\frac{s(V)}{V}, \quad (40)$$

irrespective of the number of times a cylinder is filled.

As indicated in A-1-3-5, the error is a function of temperature. At 25°C, the experimental standard deviations of the mean volumes were 2.15 and 0.99  $\text{cm}^3$  for cylinders 1 and 2, respectively, whereas the computed value was 0.60  $\text{cm}^3$ . The value 2.15  $\text{cm}^3$ , being the largest of the three, will be used as the estimate of the standard deviation for the cylinder volume.

Consider now eq. (25) where the experimental standard deviation of the mean value is used instead of the calculated standard deviation of a single volume determination. The equation becomes

$$s(V) = [(2.15)^2 + 0.0004(t - 25^\circ\text{C})^2]^{1/2}. \quad (41)$$

The maximum value of  $t - 25^\circ\text{C}$  is  $10^\circ\text{C}$  for the instrument. Then  $s(V)$  can be shown to be 2.16  $\text{cm}^3$ . The relative error is  $2.16 / (29.7 \times 10^3)$  or 0.73 parts in  $10^4$ . Since the volume error is almost independent of the bath temperature, the value 0.73 parts in  $10^4$  will be used for further calculation.



The nominal value of  $\rho$  is  $1.1 \times 10^{-3} \text{ g/cm}^3$ . The estimated  $s(\rho)$  is  $0.14 \times 10^{-6} \text{ g/cm}^3$ . The relative uncertainty in  $\rho$ , i.e.,  $s(\rho)/\rho$ , is therefore 1.3 parts in  $10^4$ .

The relative standard deviation of the mixing ratio is given by  $s(r) = [(1.3)^2 + (0.73)^2 + (2.2)^2]^{1/2}$ , in units per  $10^4$  where  $1.3 = s(\rho)$ ;  $0.73 = s(V)$ ; and  $2.2 = s(m)$ . The latter is based on collecting 0.6 gram of water. Thus  $s(r) = 2.7$  parts per  $10^4$ .

A-2-1-2 Systematic Errors in the Mixing Ratio. In addition to the systematic errors which arise in the measurements of water vapor mass, cylinder volume, and dry air density, there are three other known non-negligible systematic error sources associated with the operation of the gravimetric hygrometer. These are the incompleteness of water vapor absorption by the U-tubes, an irregular sampling flow rate coupled with a possibility of variation in the test gas moisture content, and leakage of room air into the drying train and cylinders.

Only the extremes of these errors can be estimated, although the actual error in any test could lie anywhere between zero and the extremes. Accordingly, no attempt is made to correct for these errors.

The error arising from two systematic maximum errors of the same sign is given by the algebraic sum of the two. On the other hand, systematic maximum errors of opposite signs may not be added algebraically. Rather, systematic errors of opposite signs give rise to an error band. The upper and lower error limits are not necessarily the same.

A-2-1-2-1 Systematic Errors in Mass of Water Vapor, Cylinder Volume, and Dry Gas Density. It was shown in A-1-2-9, A-1-3-6, and A-1-4-5 that the maximum possible systematic errors in the mass of water vapor, cylinder volume and gas density are respectively  $\pm 0.048 \text{ mg}$ ,  $\pm 0.48 \text{ cm}^3$ , and  $\pm 0.12 \times 10^{-6} \text{ g/cm}^3$ .

Since the nominal values of these parameters are  $m = 0.6 \text{ gram}$ ,  $V = 29.7 \text{ liter}$ , and  $\rho = 1.06 \times 10^{-3} \text{ g/cm}^3$ , the relative systematic errors, in units of parts per  $10^4$ , are  $\pm 0.80$ ,  $\pm 0.16$  and  $\pm 1.13$  (for  $m$ ,  $V$  and  $\rho$ ).

Therefore, these sources contribute a maximum systematic error in the mixing ratio of  $\pm 2.09$  parts per  $10^4$ .

A-2-1-2-2 Incompleteness of Absorption by the U-tubes. Although the data analysis of the water pick-up experiments (A-1-2-7) revealed no systematic tendencies, it was suggested that a maximum of  $0.5 \times 10^{-4} \text{ mg}$  of water vapor may go undetected for each liter of dry air collected.

The maximum duration of the water pick-up runs was nominally 8 hours at a flow of about 1.5 lpm. Thus 720 liters of air were drawn through the absorption tubes and the mass of water vapor that may have escaped absorption was at most  $0.5 \times 10^{-4} \times 720$  or 0.04 mg. If in any run the amount was less, it could easily have gone undetected.

Therefore, the experiment described in A-1-2-10 is not a conclusive basis for assuming the nonexistence of this type of systematic error, especially for tests which are more than 8 hours long, and such an error will be assumed to be present.

The nominal air density encountered during tests with the gravimetric hygrometer is 1.06 g/l. Since the maximum amount of water that may be in the effluent from the absorption tubes is  $0.5 \times 10^{-4}$  mg/l of air, the measured mixing ratio can be lower than the actual mixing ratio by at most  $0.5 \times 10^{-4}$  mg/1.06 gram or  $0.47 \times 10^{-4}$  mg/g, regardless of the magnitude of the mixing ratio.

One of the criteria for the operation of the gravimetric hygrometer is that at least 0.6 gram of water vapor shall be collected in any test. Thus a test made at a low moisture content will require a larger volume of test gas to be drawn through the U-tubes and therefore more cylinders to be filled than at a high moisture content. Assuming that the mass of air in a filled cylinder is 31.6 grams and that 0.6 gram of water vapor is collected per run, a nominal mixing ratio may be computed for a run in which a given number of cylinders are filled.

Table 17 lists examples of the number of cylinder fillings at which a run may be terminated, nominal mixing ratios in units of milligrams of water vapor per gram of associated dry air, and the relative error, E, of the mixing ratio in parts per  $10^{-4}$ , based on the relation

$$\frac{0.47 \times 10^{-4}}{r} = \frac{E}{10^4} \quad , \quad (42)$$

where r is the mixing ratio in mg/g.

The unabsorbed moisture passes into the cylinders where it is measured as dry air. Therefore the apparent measured amount of dry gas is too high by the amount of vapor present, and this again causes the measured mixing ratio to be smaller than it should be.

Since the molecular weight ratio of water to air is 0.62197, each unit mass of water vapor displaces  $1/0.62197$  or 1.608 units of air mass. Thus the  $0.5 \times 10^{-7}$  gram of water vapor per liter of dry air that flows into the cylinder causes an overstatement of the amount of dry air present by  $0.8 \times 10^{-7}$  gram for each liter present.

The relative error X in the mass of dry gas is found from the relation

$$\frac{0.8 \times 10^{-7}}{\rho} = \frac{X}{10^4} \quad , \quad (43)$$

where  $\rho$  is the nominal air density which for this calculation may be considered equal to 1 g/l. The relative error is thus  $0.8 \times 10^{-3}$  parts in  $10^4$ , which is completely negligible.

A-2-1-2-3 Flow Effect Error. At average sampling flow rates between 1 lpm and the maximum of 2 lpm, the rate is faster when a cylinder begins to fill than when it is almost full. This cyclic sampling affects neither the flow through, nor the output of, the humidity generator, which serves as the source of test gas. However, if the output of moisture content from the generator were to be cyclic during brief time periods, then the possibility arises that the sampling rate and generator output could be synchronous for such periods. Unless the total length of the run were long compared to the synchronous period, a significant systematic error in the average value of the mixing ratio as determined by the gravimetric hygrometer could result.

For example, if the hygrometer were to sample low moisture content air at 2 lpm for 10 minutes, then high moisture content air at 1 lpm for 10 minutes, it would sample 20 liters of low moisture content and only 10 liters of high moisture content, biasing the result in favor of the former.

Because the probability of synchronization is small, the averaging nature of the operation is considered to make this flow effect error negligible for runs in which the number of cylinders filled is greater than three.

For runs in which the number of cylinders filled is less than three, the effect may be eliminated by maintaining the flow at 1 lpm or less. At these lower rates, the flow can be maintained with adequate constancy. Since this is the manner in which short runs are performed, the flow effect is negligible over the entire operational range of the instrument.

Subsequent error analysis is based on a flow rate of 1 lpm, so no additional error is introduced by the flow restriction for runs in which the number of cylinders filled is less than three.

A-2-1-2-4 Leakage Error. A leakage check of both cylinders indicates a completely negligible leakage rate at pressure near 20 millitorr.

When a check is made on a system consisting of one cylinder and the pressure switch, the leakage rate decreases monotonically from 0.03 cm<sup>3</sup>/min in a pressure range of 20 to 50 millitorr to 0.02 cm<sup>3</sup>/min in a pressure range of 100 to 120 millitorr.

At a sample gas flow rate of one lpm, a constant leakage rate of 0.02 cm<sup>3</sup>/min would contribute an extra 0.02 cm<sup>3</sup> of room air to every liter of dry test gas, an error of two parts in  $10^5$  in the volume of the dried test gas. However, since the leakage rate probably decreases below 0.02 cm<sup>3</sup>/min as the pressure increases, the error it contributes to the air volume in the cylinders is considered to be negligible.



The main drying train was subjected to separate leakage tests. Air leaking into the train enters from the room, carrying water vapor that is absorbed in the U-tubes. The tests indicate approximate leakage of 0.003 cm<sup>3</sup>/min at pressures in the millitorr range, and 0.002 cm<sup>3</sup>/min at a nominal pressure of 340 Torr. This leakage apparently does not decrease appreciably with increasing pressure, and it will be assumed that the leakage rate of 0.002 cm<sup>3</sup>/min holds over the entire range of pressures. Furthermore, it will be assumed that the entire leakage occurs into the first two tubes of the main drying train, where the water vapor in the incoming room air is picked up and later weighed as part of the total water mass. The dried air from the leakage then passes on into the cylinders, where it is measured as part of the total dry air mass.

The mixing ratio is given by eq. (1). However, since there is leakage, the mixing ratio actually measured is given by

$$r = M + \rho_{wa}V'/(V\rho + V'\rho') , \quad (44)$$

where

M, V,  $\rho$  = the quantities defined for eq. (1),  
 $\rho_{wa}$  = mass of water vapor per unit volume of dry room air, g/l,  
 $\rho'$  = density of dry room air, g/l, and  
 $V'$  = volume of dry room air entering the system, l.

The mass of dry air collected per cylinder,  $V\rho$ , is about 31.6 grams and the mass of water collected per run, M, is about 0.6 gram.

If a flow rate of one lpm is assumed, then it takes 30 minutes to fill a cylinder, and the total volume of room air leaking into the drying train during the filling of each cylinder is  $6 \times 10^{-5}$  liters. Assuming the nominal room air density to be 1.17 g/l, the mass of dry air, per cylinder, from the leakage into the absorption tubes is  $1.17 \times 6 \times 10^{-5}$  gram or  $7.02 \times 10^{-5}$  gram.

To assess the quantity  $\rho_{wa}V'$ , the water vapor mass from the room air that is collected in the U-tubes, it is necessary to consider conditions of both maximum and minimum water vapor density in the ambient air in the vicinity of the drying train.

The lowest temperature in the area in which the hygrometer is used may be about 19°C. A room relative humidity of 10 percent is assumed possible at this temperature. At this temperature, the saturation concentration of water vapor in air is  $16.31 \times 10^{-3}$  gram of water vapor per liter of air, so that at a relative humidity of 10 percent, the concentration is  $1.631 \times 10^{-3}$  gram of water vapor per liter of air. Since  $6 \times 10^{-5}$  liters of room air leak into the system per cylinder,  $1.631 \times 6 \times 10^{-8}$  or  $9.8 \times 10^{-8}$  gram of water vapor are collected from the leakage for each cylinder filling.

The highest ambient temperature is 28°C, with a possible relative humidity of 60 percent. The saturation concentration is  $27.24 \times 10^{-3}$  gram of water vapor per liter of air, so that at a relative humidity of 60 percent, the concentration is  $16.344 \times 10^{-3}$  gram of water vapor per liter of air. Thus  $6 \times 10^{-5} \times 16.344 \times 10^{-3}$  or  $98.1 \times 10^{-8}$  gram of water vapor is collected from

the leakage, for each cylinder.

In table 18 are tabulated the masses of air and water gained from both the test gas and the leakage gas under the conditions of maximum and minimum observed water vapor density in the ambient air, for tests involving different numbers of cylinder fillings.

Table 19 is a continuation of table 18 in which the "true" mixing ratio (based on the assumptions of collecting 0.6 gram water vapor per run and that the mass of associated dry air per cylinder is 31.6 grams), and the measured mixing ratio (assuming leakage in addition to the above) are given, along with the relative systematic error.

The mixing ratios have been computed to as many figures as was necessary to get an error indication. The ratios are listed in terms of mg/g. When the room air mixing ratio is less than the test gas mixing ratio, the error sign is negative, and for the inverse situation, the error sign is positive.

### A-3 OVERALL ERROR IN MIXING RATIO

The discussion of systematic errors in the mixing ratio was based on estimates of the maximum contributions to the systematic uncertainty in a mixing ratio determination expected from various parameters.

It was shown in A-2-1-1 that random errors gave rise to a relative standard deviation of the mixing ratio of 2.7 parts in  $10^4$ . The maximum contribution of the random errors to the uncertainty in a mixing ratio determination is considered to be three standard deviations or  $\pm 8.1$  parts in  $10^4$ .

Examples of runs in which a given number of cylinders are filled are listed in table 20, along with the corresponding nominal mixing ratios, and the maximum relative errors and their sources.

For any run, the maximum negative and positive limits of error may be determined by summing separately the negative errors and the positive errors. Consider a run in which only 0.7 of a cylinder is filled, as an example. The negative errors listed in table 20, in units of parts in  $10^4$  were -8.1, -2.09, -0.017 and -0.02, the sum of which is nominally -10.2. This defines the lower error limit in this case. The positive errors are 8.1 and 2.09, the sum of which is nominally +10.2. This defines the upper error limit.

Therefore, for a run in which only 0.7 of a cylinder is filled, the error in mixing ratio will lie in the band from -10.2 to +10.2 parts in  $10^4$ . Similar calculations may be made for runs involving any number of cylinder fillings. A synopsis of such calculations is presented in table 21.

### A-4 CONCLUSIONS AND DISCUSSIONS

The National Institute of Standards and Technology (formerly National Bureau of Standards) has developed a hygrometer for the measurement of mixing

ratios lying in the range from 27 to 0.19 mg/g.

The highest measurable value is determined by consideration of operator comfort. An ambient room temperature of slightly above 30°C is tolerable for short periods, and to prevent condensation in the line, the room temperature must be above the dew-point temperature. This limits the upper dew point of the test gas to 30°C, corresponding to a mixing ratio of nominally 27 mg/g, although the hygrometer itself is capable of measuring a higher value.

The lower limit, 0.19 mg/g, is determined primarily by error considerations, since it is seen that systematic errors from leakage and incomplete absorption become important in this range.

The estimated maximum error magnitude encountered over the operational range of the instrument is 12.7 parts in  $10^4$ , or 0.13 percent of the measured value.

## B. NBS TWO-PRESSURE HUMIDITY GENERATOR

A precision humidity generator [28] is used as the principal facility for calibrating transfer and secondary standards, and for testing and evaluating hygrometers and sensors. The generator operates on what is now known as the two-pressure principle. A stream of air at an elevated pressure is saturated with respect to the liquid or solid phase of water and then expanded to a lower pressure. Measurements of the pressure and temperature of the saturated air stream, and in the test chamber after expansion, yield the data necessary to compute the water vapor content of the air stream.

The calibration of a hygrometer with the two-pressure humidity generator can be made in various units which relate to the quantity of water vapor in a moist air. Among the most common units are mixing ratio, dew-point temperature, relative humidity, and volume ratio. These expressions are defined in terms of real gas behavior and account for the fact that the saturation pressure of pure water in the presence of an inert gas differs from that of pure water alone.

### B-1 COMPUTATIONS OF HUMIDITY

The saturation mixing ratio,  $r_w$ , of the moist gas emerging from the generator is

$$r_w = \frac{M_w f(P_s, T_s) e_w(T_s)}{M_g [P_s - f(P_s, T_s) e_w(T_s)]} , \quad (45)$$



where

$M_w$  = molecular weight of water vapor,  
 $M_g$  = molecular weight of the carrier gas,  
 $e_w(T_s)$  = saturation vapor pressure over a plane surface of the pure phase of liquid or solid water at the saturator temperature,  $T_s$ ,  
 $P_s$  = saturator pressure, and  
 $f$  = enhancement factor and is defined below.

The enhancement factor,  $f$ , at the saturator pressure,  $P_s$ , and temperature,  $T_s$ , is expressed by

$$f(P_s, T_s) = \frac{x_w P_s}{e_w(T_s)} = \frac{(1-x_g) P_s}{e_w(T_s)}, \quad (46)$$

where  $x_g$ ,  $x_w$  = the mole fractions of carrier gas and water vapor in the saturated mixture, respectively.

The definition of the relative humidity RH in percent in the test chamber of the generator is expressed by

$$RH = (x_v/x_w)_{P_c, T_c} \times 100, \quad (47)$$

where  $x_v$  = the mole fraction of water vapor in a given sample of moist air characterized by pressure,  $P_c$ , and temperature,  $T_c$ , and  $x_w$  = the mole fraction of water vapor in the saturated mixture at the same values of pressure and temperature.

Substituting appropriate expressions for the mole fractions yields

$$RH = \frac{f(P_s, T_s)}{f(P_c, T_c)} \times \frac{e_w(T_s)}{e_w(T_c)} \times \frac{P_c}{P_s} \times 100, \quad (48)$$

where  $f(P_c, T_c)$  = enhancement factor at test chamber pressure,  $P_c$ , and temperature  $T_c$ ,

$e_w(T_c)$  = saturation vapor pressure over a plane surface of the pure phase of liquid or solid water at the test chamber temperature,  $T_c$ .

The "thermodynamic dew-point (or frost-point) temperature"  $T_d$  of a moist gas at absolute total pressure,  $P$ , is defined as that temperature at which the moist gas is saturated with respect to a plane surface of pure liquid (or solid) water. The dew point,  $T_d$ , of the moist gas of the two-pressure generator is obtained by the iterative solution of

$$f(P_c, T_d)e_w(T_d) = f(P_s, T_s)e_w(T_s)P_c/P_s, \quad (49)$$

where  $e_w$  and  $f$  are values obtained from suitable tables and  $P_c$  is the absolute pressure in any space or volume that is filled with the moist gas, e.g., the mirror chamber of a dew-point hygrometer.

The volume ratio,  $V$ , of the moist gas of the two-pressure generator is

$$V = \frac{f(P_s, T_s)e_w(T_s)}{P_s - f(P_s, T_s)e_w(T_s)} \quad (50)$$

Hence, with the establishment of constant temperature and pressures in the saturator and test chamber the various units of humidity can be calculated for the moist gas produced by the two-pressure humidity generator. The formulations of Wexler [29,30] are used for obtaining the saturation vapor pressure of water and ice. When air is used as the carrier gas, the values for the enhancement factor,  $f$ , for air, given by Hyland [31] over the temperature range  $-50^\circ$  to  $90^\circ\text{C}$  and pressures from  $0.25 \times 10^5$  to  $10^7$  Pa are used in the above equations. Greenspan [32] has obtained a simplified equation for  $f$  which can be easily programmed for a computer or can be calculated with the aid of a programmable pocket calculator.

Since both dew/frost point and relative humidity can be expressed with respect to either ice or water, appropriate functions for the enhancement factor and the saturation vapor pressure are required in eqs. (48) and (49) for computations.

Intercomparison tests were made with the NBS standard gravimetric hygrometer [1] over a portion of the generator's operating range. The estimated maximum uncertainty (three standard deviations) is 0.2 percent RH for temperatures between  $0^\circ$  to  $80^\circ\text{C}$  which, in units of dew point, corresponds to an estimated maximum uncertainty of  $0.04^\circ\text{C}$  for dew points from  $-35$  to  $80^\circ\text{C}$ .

## B-2 ANALYSIS OF COMPONENT SYSTEMS

As indicated in eqs. 45 through 50, the calculations of the various units of humidity require the measurement of the temperatures and pressures of the final saturator and the test chamber.

To facilitate the automation of data acquisition, the resistances of the calibrated four-lead standard platinum resistance thermometer and the calorimetric type platinum resistance thermometer are measured with a bridge based on a design by Cutkosky [33]. The bridge utilizes an inductive ratio divider and requires only one adjustment for balancing. A built-in phase-sensitive null-detector easily resolves  $1 \mu\Omega$  in  $25 \Omega$ . Small deviations from balance are recorded continuously with an analog recorder and/or the BCD output of a digital voltmeter is recorded on a line printer at any preselected time interval. The platinum resistance thermometers were calibrated at NBS on the International Practical Temperature Scale of 1968 and subsequently checked

from time to time at the triple point of water. It is estimated that the uncertainty in the temperature measurement is an order of magnitude more accurate than the required 10 millidegree Celsius in order to maintain an accuracy of 0.2% for most of the mixing ratio range.

The pressures are measured with calibrated fused quartz Bourdon tube pressure gages equipped with BCD outputs. The ranges of the pressure gages used in the generator are 0 to 0.21 MPa (30.5 psia) for the test chamber and 0 to 0.69 MPa (100 psia) or 0 to 3.45 MPa (500 psig) for the saturator. These gages are periodically calibrated with a dead weight piston gage. The accuracy of the pressure measurement is estimated at 70 Pa. This has been taken into account in the overall random and systematic errors.

### B-3 ANALYSIS OF COMPLETE SYSTEM

Two independent approaches were used to evaluate the performance of this generator. First, an intercomparison was made between the generator and the NIST Standard Hygrometer. Second, an analysis was made of all known possible sources of error and from this analysis, an estimate was derived for the accuracy that could be expected from the generator. The results of the two methods were compared.

#### B-3-1 INTERCOMPARISON TESTS

A 3x3 Graeco-latin square experiment [34] was used to test four variable parameters of the two-pressure humidity generator. The experiment was designed to determine whether any of the preselected levels of the parameters could affect the accuracy of the generator. The four parameters which were tested in the experiment were the presaturator temperature, the final saturator temperature, the pressure of the saturator, and the test gas (air) flow.

Three levels for each of the four parameters were used in the test.

The parameters were arranged in the following form:

$T_{-20}, \Delta t_0, P_2, F_{10}$	$T_0, \Delta t_5, P_5, F_{10}$	$T_{25}, \Delta t_{15}, P_1, F_{10}$
$T_{-20}, \Delta t_5, P_1, F_5$	$T_0, \Delta t_{15}, P_2, F_5$	$T_{25}, \Delta t_0, P_5, F_5$
$T_{-20}, \Delta t_{15}, P_5, F_1$	$T_0, \Delta t_0, P_1, F_1$	$T_{25}, \Delta f_5, P_2, F_1$



where

- $T$  = the final saturator temperature and  $T_{-20} = -20^{\circ}\text{C}$ ,  $T_0 = 0^{\circ}\text{C}$ ,  $T_{25} = 25^{\circ}\text{C}$ ;  
 $\Delta t$  = the difference in the temperature between the presaturator and the final saturator, the subscript indicating the amount in degrees Celsius that the former exceed the latter;  
 $P$  = the final saturator pressure and  $P_1 = 10^5 \text{ Pa}$ ,  $P_2 = 2 \times 10^5 \text{ Pa}$ ,  $P_5 = 5 \times 10^5 \text{ Pa}$ ; and  
 $F$  = the rate of test air flow and  $F_1 = .03 \text{ m}^3/\text{min}$ ,  $F_5 = .15 \text{ m}^3/\text{min}$ ,  $F_{10} = .3 \text{ m}^3/\text{min}$  (at  $25^{\circ}\text{C}$  and  $10^5 \text{ Pa}$ ).

Each entry of the Graeco-latin square represents a run and the four parameters were maintained at the designated levels. The mixing ratio of the moist air produced by the two-pressure generator was calculated by using eq. (45) for each of the runs and the results were compared with the value of the mixing ratio as measured by the NIST Standard Hygrometer. The NBS Standard Hygrometer has a maximum uncertainty of 0.13 percent.

#### B-3-1-1 RESULTS

A percentage difference,  $d$ , was obtained by using the expression  $d = (r_w - r_g)/r_g \times 100$  where  $r_w$  is the computed mixing ratio for the generator and  $r_g$  is the mixing ratio measured by the NIST standard hygrometer. The results of the tests for the  $3 \times 3$  Graeco-latin square experiment are given in table 22. Two values in a box represent a repeat run.

In the first column of table 22,  $T_{-20}$  is the value of the parameter,  $T$ , common to all three boxes in that column while the other three parameters are each represented at the three different levels indicated. Similarly,  $T_0$  and  $T_{25}$  are the values of the parameter,  $T$  common to all boxes in columns two and three, respectively. If the four tested parameters are assumed to be independent of each other and have no interactions, then the average value in each column is indicative of the correlation of the percentage difference,  $d$ , with the value of  $T$  for that column. Similar analyses of the rows yield the correlation of  $d$  with  $F$ , analyses of one set of diagonals give the correlation of  $d$  with  $P_2$ , while analyses of the second set of diagonals give the correlation of  $d$  with  $\Delta t$ . These results are given in table 23.

In order to assess the significance of  $d$  in table 23, it is necessary to remember that the maximum uncertainty in  $r_g$  is 0.13 percent. Therefore, if  $d$  exceeds 0.13 percent, the increase is ascribed to  $r_w$  and, more particularly, to the corresponding parameter level.

#### B-3-2 ERROR ANALYSIS

An estimate of the maximum uncertainty in the calculated mixing ratio,  $r_w$ , of the generator for each of the runs was obtained by using the estimated systematic uncertainty plus three times the random uncertainty of the measured pressure and temperature in the final saturator. The maximum uncertainty of the enhancement factor, which also includes the uncertainty in the saturation vapor pressure values, was obtained from table 9 of Hyland's paper [31]. The

standard deviations were computed for the measured temperature and pressure of the saturator in each of the runs and the standard deviation of the mean was used as a measure of the random uncertainty. The systematic uncertainty in the pressure measurement was attributed to the uncertainty in the calibration of the pressure gage, and for the temperature measurement, the systematic uncertainty was primarily due to the maximum temperature gradient detected in the final bath, which contains the saturator and the test chamber. The estimated uncertainty in the calculated mixing ratio was obtained from the expression:

$$\frac{\Delta r_w}{r_w} = \frac{P_s}{P_s - f e_w} \left[ \left( \frac{\Delta e_w}{e_w} \right)^2 + \left( \frac{\Delta P_s}{P_s} \right)^2 + \left( \frac{\Delta f}{f} \right)^2 \right]^{1/2} . \quad (51)$$

Table 24 lists the estimated systematic uncertainty and the 3 $\sigma$  errors for each of the runs and also the estimated maximum uncertainty in the generator.

By inserting the values of the estimated maximum uncertainty given in table 24 in the appropriate squares of the 3x3 Graeco-latin square and by computing the mean for each row, column and diagonal of the square, the results obtained are a measure of the estimated maximum uncertainty of the generator for each level of the tested parameters. These results are given in table 25.

Comparison of the results (to the nearest tenth of a percent) of tables 23 and 25 show that the calculated maximum uncertainty of the generator is equal to or greater than the percentage difference  $d$  for the various levels of the tested parameters and therefore it may be concluded that the performance of the generator is not affected by the four tested parameters over the range in which these parameters were tested.

#### B-4 SUMMARY OF UNCERTAINTY QUOTE FOR THE NIST TWO-PRESSURE HUMIDITY GENERATOR, MARK 2

The results of the intercomparison tests of the generator with the standard hygrometer which are shown in the previous section indicate that the estimated maximum uncertainty of the generator (based on the systematic and 3 $\sigma$  uncertainties of the temperature and pressure measurements and the maximum error for the enhancement factor) are equal to or greater than the measured difference,  $d$ . Therefore, similar calculations were made beyond the range covered by the intercomparison tests to obtain the estimates of the maximum uncertainty for the generator over the temperature range of -55 to 80°C and for pressures from ambient to 3.3 x 10<sup>6</sup> Pa. Table 26 lists these results which are given in units of mixing ratio, volume ratio, dew-point temperature, and relative humidity.

#### B-5 SURVEILLANCE

As stated in Section B-2, the calculations of the various units of humidity require the measurement of the temperatures and pressures in the final saturator and the test chamber.

To assure that the accuracy of the temperature measurements are maintained, the  $R_0$  (ice point resistances) of the platinum resistance thermometers are redetermined at six month intervals through use of a triple point of water cell. If the thermometer reading deviates a few millidegrees from the calibrated value, the thermometer is returned to the Temperature Standards Group for recalibration.

It has been determined that by checking the zero of the pressure gages each month, the required accuracy for the pressure measurements is maintained. In addition, the gages are checked once a year against a calibrated dead weight piston gage.

In addition, tests are continuously made to check the overall performance of the generator. An example of such a test is to maintain a constant temperature and pressure in the final saturator and to vary the external saturator temperature. If a hygrometer with high sensitivity indicates no change in the output, the test indicates satisfactory operation of the saturation system. Similar tests are made to determine the independence of the generator to air flow rates and presaturator water level.

Although there were no indications regarding the malfunctioning of the generator after a period of ten years since the original test, an intercomparison test of the generator was recently made with the NIST Standard Hygrometer. The test was performed at a mixing ratio of 10 mg/g and the predicted mixing ratio of the generator agreed to within .01 percent of the measured mixing ratio of the gravimetric hygrometer. The result of the intercomparison test reconfirmed that the overall operation of the generator has not changed.



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Table 1. Standard deviation of the air density for water vapor mass determination.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial \rho}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right)s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right)^2 s^2(z_n)$
T	$3.9 \times 10^{-6} \text{g/cm}^3/\text{K}$	0.07K	$0.27 \times 10^{-6} \text{g/cm}^3$	$0.0729 \times 10^{-12} \text{g}^2/\text{cm}^6$
B	$1.6 \times 10^{-6} \text{g/cm}^3/\text{mmHg}$	0.09 mmHg	$0.14 \times 10^{-6} \text{g/cm}^3$	$0.0196 \times 10^{-12} \text{g}^2/\text{cm}^6$
RH	$0.15 \times 10^{-6} \text{g/cm}^3/\% \text{RH}$	0.7%RH	$0.10 \times 10^{-6} \text{g/cm}^3$	$0.0100 \times 10^{-12} \text{g}^2/\text{cm}^6$
$e_s$	$0.24 \times 10^{-6} \text{g/cm}^3/\text{mmHg}$	0.09 mmHg	$0.022 \times 10^{-6} \text{g/cm}^3$	$0.0005 \times 10^{-12} \text{g}^2/\text{cm}^6$

$$s^2(\rho) = 0.1030 \times 10^{-12} \text{g}^2/\text{cm}^6$$

$$s(\rho) = 0.32 \times 10^{-6} \text{g/cm}^3$$



Table 2. Standard deviation of external u-tube volume.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial V_o}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial V_o}{\partial z_n}\right)s(z_n)$	$\left(\frac{\partial V_o}{\partial z_n}\right)^2 s^2(z_n)$
$\rho_1$	$53.9\text{cm}^6/\text{g}$	$0.42 \times 10^{-6}\text{g}/\text{cm}^3$	$22.6 \times 10^{-6}\text{cm}^3$	negligible
$\rho_2$	$3.8\text{cm}^6/\text{g}$	$0.42 \times 10^{-6}\text{g}/\text{cm}^3$	$1.7 \times 10^{-6}\text{cm}^3$	negligible
$d_1$	$2.6\text{cm}^6/\text{g}$	$45 \times 10^{-6}\text{g}/\text{cm}^3$	$117 \times 10^{-6}\text{cm}^3$	negligible
$d_2$	$68.1\text{cm}^6/\text{g}$	$45 \times 10^{-6}\text{g}/\text{cm}^3$	$3064 \times 10^{-6}\text{cm}^3$	$9.4 \times 10^{-6}\text{cm}^6$
$W_1$	$1.0\text{cm}^3/\text{g}$	$0.013\text{g}$	$0.013\text{cm}^3$	$169 \times 10^{-6}\text{cm}^6$
$W_2$	$1.0\text{cm}^3/\text{g}$	$0.010\text{g}$	$0.010\text{cm}^3$	$100 \times 10^{-6}\text{cm}^6$

$$s^2(V_o) = 278 \times 10^{-6}\text{cm}^6$$

$$s(V_o) = 0.017\text{cm}^3$$

Table 3. Standard deviation of the buoyancy correction for the water vapor mass determination.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial C_b}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial C_b}{\partial z_n}\right)s(z_n)$	$\left(\frac{\partial C_b}{\partial z_n}\right)^2 s^2(z_n)$
$\rho_i$	$11.36\text{cm}^3$	$0.32 \times 10^{-6}\text{g/cm}^3$	$3.635 \times 10^{-6}\text{g}$	$13.213 \times 10^{-12}\text{g}^2$
$\rho_f$	$11.36\text{cm}^3$	$0.32 \times 10^{-6}\text{g/cm}^3$	$3.635 \times 10^{-6}\text{g}$	$13.213 \times 10^{-12}\text{g}^2$
$V_T$	$10^{-4}\text{g/cm}^3$	$0.04\text{cm}^3$	$4.00 \times 10^{-6}\text{g}$	$16.000 \times 10^{-12}\text{g}^2$
$V_U$	$10^{-4}\text{g/cm}^3$	$0.04\text{cm}^3$	$4.00 \times 10^{-6}\text{g}$	$16.000 \times 10^{-12}\text{g}^2$
$W_{Li}$	0.00015	$5.2 \times 10^{-6}\text{g}$	Negligible	Negligible
$W_{Lf}$	0.00015	$5.2 \times 10^{-6}\text{g}$	Negligible	Negligible
$W_{Si}$	0.00014	$10^{-6}\text{g}$	Negligible	Negligible
$W_{Sf}$	0.00014	$10^{-6}\text{g}$	Negligible	Negligible

$$s^2(C_b) = 58.426 \times 10^{-12}\text{g}^2$$

$$s(C_b) = 7.6 \times 10^{-6}\text{g}$$

Table 4. Standard deviation of hydrogen density in sealed U-tube.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial \rho_h}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho_h}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial \rho_h}{\partial z_n}\right)^2 s^2(z_n)$
T	$0.27 \times 10^{-6} \text{g/cm}^3/\text{K}$	0.07K	$1.9 \times 10^{-8}$	$3.6 \times 10^{-16} \text{g}^2/\text{cm}^6$
B	$0.11 \times 10^{-6} \text{g/cm}^3/\text{mmHg}$	0.06mmHg	$0.66 \times 10^{-8}$	$0.44 \times 10^{-16} \text{g}^2/\text{cm}^6$

$$s^2(\rho_h) = 4.0 \times 10^{-16} \text{g}^2/\text{cm}^6$$

$$s(\rho_h) = 2 \times 10^{-8} \text{g/cm}^3$$



Table 5. Standard deviation of initial U-tube volume.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial V_i}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial V_i}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial V_i}{\partial z_n}\right)^2 s^2(z_n)$
$W_a$	$0.93 \times 10^3 \text{cm}^3/\text{g}$	$80 \times 10^{-6} \text{g}$	$74 \times 10^{-3} \text{cm}^3$	$5476 \times 10^{-6} \text{cm}^6$
$W_h$	$0.93 \times 10^3 \text{cm}^3/\text{g}$	$80 \times 10^{-6} \text{g}$	$74 \times 10^{-3} \text{cm}^3$	$5476 \times 10^{-6} \text{cm}^6$
$\rho_a$	$2.9 \times 10^4 \text{cm}^6/\text{g}$	$0.29 \times 10^{-6} \text{g}/\text{cm}^3$	$8 \times 10^{-3} \text{cm}^3$	$64 \times 10^{-6} \text{cm}^6$
$\rho_h$	$2.9 \times 10^4 \text{cm}^6/\text{g}$	$0.02 \times 10^{-6} \text{g}/\text{cm}^3$	$0.6 \times 10^{-3} \text{cm}^3$	Negligible

$$s^2(V_i) = 11016 \times 10^{-6} \text{cm}^6$$

$$s(V_i) = 0.11 \text{cm}^3$$

Table 6. Standard deviation of the correction for mass of internal gas.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial C_g}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial C_g}{\partial z_n}\right)s(z_n)$	$\left(\frac{\partial C_g}{\partial z_n}\right)^2 s^2(z_n)$
$V_i$	$1 \times 10^{-4} \text{g/cm}^3$	$0.11 \text{cm}^3$	$1.1 \times 10^{-5} \text{g}$	$1.2 \times 10^{-10} \text{g}^2$
$v^*$	$1.17 \times 10^{-3} \text{g/cm}^3$	$0.066 \text{cm}^3$	$7.7 \times 10^{-5} \text{g}$	$59.3 \times 10^{-10} \text{g}^2$
$\rho_f$	$30 \text{cm}^3$	$0.29 \times 10^{-6} \text{g/cm}^3$	$9 \times 10^{-6} \text{g}$	$0.8 \times 10^{-10} \text{g}^2$
$\rho_i$	$29.5 \text{cm}^3$	$0.29 \times 10^{-6} \text{g/cm}^3$	$9 \times 10^{-6} \text{g}$	$0.8 \times 10^{-10} \text{g}^2$

$$s^2(C_g) = 62.1 \times 10^{-10} \text{g}^2$$

$$s(C_g) = 7.9 \times 10^{-5} \text{g}$$

\*In the case of the second and third tubes, the error in  $v$  has been shown to be negligible. For these tubes, it can be shown that  $s(C_g) = 1.7 \times 10^{-5} \text{g}$ .

Table 7. Standard deviation of the mass of water collected in a u-tube\*.

Independent Variable	Standard Deviation	Variance
$z_n$	$s(z_n)$	$s^2(z_n)$
$W_f$	$11 \times 10^{-6}g$	$121 \times 10^{-12}g^2$
$W_i$	$11 \times 10^{-6}g$	$121 \times 10^{-12}g^2$
$C_w$	$7.5 \times 10^{-6}g$	$56 \times 10^{-12}g^2$
$C_b$	$7.6 \times 10^{-6}g$	$58 \times 10^{-12}g^2$
$C_a$	Negligible	Negligible
$C_g^{**}$	$79 \times 10^{-6}g$	$6241 \times 10^{-12}g^2$

$$s^2(m) = 6597 \times 10^{-12}g^2$$

$$s(m) = 81 \times 10^{-6}g$$

\*The error arising from the non-application of  $C_i$  is considered on p. 423.

\*\*Note that there is another case, where  $s(C_g)$  is  $1.7 \times 10^{-5}g$  (see Table 6). In that case, it can be shown that  $s(m) = 25 \times 10^{-6}g$ .



Table 8. Dry runs - estimate of the accuracy of the weight gain of a single tube.

Tube No.	Run No.	Average U-Tube Weight* (mg x 10 <sup>2</sup> )	Difference in Average Weight (mg x 10 <sup>2</sup> )	(Difference) <sup>2</sup> (mg <sup>2</sup> x 10 <sup>4</sup> )	Degrees of Freedom
11		19			
	1	35	+16	256	
	2	25	-10	100	
	3	30	+ 5	25	
	4	16	-14	196	
	5	17	+ 1	1	
	6	17	0	0	5
12		19			
	7	23	+ 4	16	
	8	29	+ 6	36	
	9	34	+ 5	25	
	10	28	- 6	36	
	11	23	- 5	25	
	12	21	- 2	4	5
14		13			
	13	14	+ 1	1	
	14	8	- 6	36	
	15	9	+ 1	1	2

$$\Sigma(\text{Difference})^2 = 758 \quad \Sigma = 12$$

$$\text{Variance} = \frac{758}{12} = 632 \times 10^{-4} \text{mg}^2$$

$$\text{Standard Deviation} = 8.0 \times 10^{-2} \text{mg}$$

\*Only the final significant figures are given since only these changed from run to run.

Table 9. Moisture pick-up experiment.

Run No.	Length of Run (min.)	Tube No.	Change in Mass*	Difference Between the Mass Increase in the Drying Train and the Mass Decrease in the Water Source+++ (mg x 10 <sup>2</sup> )	(Difference) <sup>2</sup> (mg <sup>2</sup> x 10 <sup>4</sup> )
1	225	14** 11+	+1.12445 <u>+ .00107</u> +1.12552		
		15++	-1.12532	+20	400
2	225	14** 11+	+1.09609 <u>+ .01721</u> +1.11330		
		15++	-1.11349	-19	361
3	300	14** 11+	+1.15937 <u>+ .01015</u> +1.16952		
		13++	+1.16950	+ 2	4
4	296	J** R+	+ .74388 <u>+ .00011</u> + .74399		
		A++	- .74407	- 8	64
5	490	B** J+	+1.26387 <u>+ .00008</u> +1.26395		
		R++	-1.26381	+14	196

$$\Sigma = 1025\text{mg}^2 \times 10^{-4}$$

$$\text{Variance} = 256\text{mg}^2 \times 10^{-4}$$

$$\text{Standard Deviation} = 16\text{mg} \times 10^{-2}$$

\*Based on average of two to five weighings before and after the run.

\*\*First tube in drying train.

+Second tube in drying train.

++Water source.

+++Plus sign indicates drying train mass increase was greater than the water source mass decrease.

Table 10. Internal volumes of cylinders at 250°C.

Run No.	Cylinder No. 1		Cylinder No. 2	
	Volume, $V_o$ ( $\text{cm}^3$ )	Deviation from Mean ( $\text{cm}^3$ )	Volume, $V_o$ ( $\text{cm}^3$ )	Deviation from Mean ( $\text{cm}^3$ )
2	29658.8	-2.2	29734.2	-0.8
3	29647.6*	-	29732.9	-2.1
4	29654.0	-7.0	29736.6	+1.6
5	29661.4**	+0.4	29738.1	+3.1
6	29665.5	+4.5	29733.4	-1.6
7	29665.3	+4.3	-	-
Mean	29661.0	$\pm 3.68$	29735.0	$\pm 1.84$
Standard deviation of the mean		$\pm 2.15$		0.99
Maximum		-7.0		+3.1

\*Air trapped in cylinder. This value was not used to compute mean.

\*\*Corrected for water trapped in vacuum exhaust valve.

Table 11. Standard deviation of the buoyancy correction in the cylinder volume determination.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial C_b}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial C_b}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial C_b}{\partial z_n}\right)^2 s^2(z_n)$
$\rho_1$	$280\text{cm}^3$	$0.42 \times 10^{-6}\text{g/cm}^3$	$0.000\text{g}$	$0.000000\text{g}^2$
$\rho_f$	$26,420\text{cm}^3$	$0.42 \times 10^{-6}\text{g/cm}^3$	$0.011\text{g}$	$0.000121\text{g}^2$
$\rho_{\text{H}_2\text{O}}$	$34.5\text{cm}^3$	$45 \times 10^{-6}\text{g/cm}^3$	$0.002\text{g}$	$0.000004\text{g}^2$
$W_f$	$1.00103$	$0.050\text{g}$	$0.050\text{g}$	$0.002500\text{g}^2$
$W_i$	$1.00964$	$0.100\text{g}$	$0.101\text{g}$	$0.010201\text{g}^2$

$$s^2(C_b) = 0.012826\text{g}^2$$

$$s(C_b) = 0.113\text{g}$$



Table 12. Standard deviation of the mass of water used in the cylinder calibration.

Independent Variable $z_n$	Standard Deviation $s(z_n)$	Variance $s^2(z_n)$
$W_f$	0.040g	$0.001600g^2$
$W_i$	0.020g	$0.000400g^2$
$C_w$	0.030g	$0.000900g^2$
$C_r$	0.005g	$0.000025g^2$
$C_b$	0.113g	$0.012770g^2$

$$s^2(M) = 0.015695g^2$$

$$s(M) = 0.125g$$

Table 13. Standard deviation of the cylinder volume at the calibration temperature.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial V_c}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial V_c}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial V_c}{\partial z_n}\right)^2 s^2(z_n)$
M	1 cm <sup>3</sup> /g	0.125g	0.125cm <sup>3</sup>	0.0157cm <sup>6</sup>
d	29.6 x 10 <sup>3</sup> g	45 x 10 <sup>-6</sup> g/cm <sup>3</sup>	1.33cm <sup>3</sup>	1.77cm <sup>6</sup>

$$s^2(V_c) = 1.79\text{cm}^6$$

$$s(V_c) = 1.34\text{cm}^3$$

Table 14. Standard deviation of the cylinder volume correction to a standard temperature.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial C_x}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial C_x}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial C_x}{\partial z_n}\right)^2 s^2(z_n)$
$V_c$	$93 \times 10^{-6} \text{cm}^3/\text{cm}^3$	$1.34 \text{cm}^3$	$0.000 \text{cm}^4$	$0.0000 \text{cm}^6$
$\alpha$	$59.4 \times 10^3 \text{cm}^3/^\circ\text{C}$	$0.45 \times 10^{-6} \text{cm}^3/\text{cm}^3/^\circ\text{C}$	$0.027 \text{cm}^3$	$0.0007 \text{cm}^6$
$t_c$	$1.38 \text{cm}^3/^\circ\text{C}$	$0.1^\circ\text{C}$	$0.138 \text{cm}^3$	$0.0190 \text{cm}^6$

$$s^2(C_x) = 0.0197 \text{cm}^6$$

$$s(C_x) = 0.14 \text{cm}^3$$

Table 15. Standard deviation of  $\rho_o$ .

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial \rho_o}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho_o}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial \rho_o}{\partial z_n}\right)^2 s^2(z_n)$
%N <sub>2</sub>	$1.25064 \times 10^{-3} \text{g/cm}^3$	0.00004	$5.0026 \times 10^{-8} \text{g/cm}^3$	$25.026 \times 10^{-16} \text{g}^2/\text{cm}^6$
%O <sub>2</sub>	$1.42848 \times 10^{-3} \text{g/cm}^3$	0.00002	$2.8570 \times 10^{-8} \text{g/cm}^3$	$8.162 \times 10^{-16} \text{g}^2/\text{cm}^6$
%CO <sub>2</sub>	$1.96465 \times 10^{-3} \text{g/cm}^3$	0.00004	$7.8586 \times 10^{-8} \text{g/cm}^3$	$61.758 \times 10^{-16} \text{g}^2/\text{cm}^6$
%A	$1.78533 \times 10^{-3} \text{g/cm}^3$	0.00001	$1.7853 \times 10^{-8} \text{g/cm}^3$	$3.187 \times 10^{-16} \text{g}^2/\text{cm}^6$
M <sub>a</sub>	$2.678 \times 10^{-8} \text{cm}^{-3}$	$6 \times 10^{-4} \text{g}$	$16.0680 \times 10^{-12} \text{g/cm}^3$	Negligible
V	$5.769 \times 10^{-8} \text{g/cm}^6$	$0.9 \text{cm}^3$	$5.1921 \times 10^{-8} \text{g/cm}^3$	$26.958 \times 10^{-16} \text{g}^2/\text{cm}^6$

$$s^2(\rho_o) = 0.0125 \times 10^{-12} \text{g}^2/\text{cm}^6$$

$$s(\rho_o) = 0.1 \times 10^{-6} \text{g/cm}^3$$



Table 16. Standard deviation of the density of air in a cylinder.

Ind. Var.	Partial Derivative	Standard Deviation		Variance
$z_n$	$\frac{\partial \rho}{\partial z_n}$	$s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right) s(z_n)$	$\left(\frac{\partial \rho}{\partial z_n}\right)^2 s^2(z_n)$
Z	$1.09 \times 10^{-3} \text{g/cm}^3$	$54 \times 10^{-6}$	$58.9 \times 10^{-9} \text{g/cm}^3$	$0.0035 \times 10^{-12} \text{g/cm}^6$
$\rho_0$	0.844	$0.1 \times 10^{-6} \text{g/cm}^3$	$0.0844 \times 10^{-6} \text{g/cm}^3$	$0.0071 \times 10^{-12} \text{g/cm}^6$
T	$3.67 \times 10^{-6} \text{g/cm}^3 \text{K}$	0.008K	$0.029 \times 10^{-6} \text{g/cm}^3$	$0.0008 \times 10^{-12} \text{g/cm}^6$
B	$1.57 \times 10^{-6} \text{g/cm}^3 / \text{mmHg}$	0.06 Torr	$0.09 \times 10^{-6} \text{g/cm}^3$	$0.0081 \times 10^{-12} \text{g/cm}^6$

$$s^2(\rho) = 0.0195 \times 10^{-12} \text{g}^2/\text{cm}^6$$

$$s(\rho) = 0.14 \times 10^{-6} \text{g/cm}^3$$

Table 17. Relative systematic error in mixing ratio from incomplete water absorption\*.

No. of Cylinders	Nominal Mixing Ratio (mg/g)	Relative Error (parts/10 <sup>4</sup> )
0.7	27.1	-0.017
1	18.9	-0.025
10	1.89	-0.25
40	0.475	-0.99
100	0.189	-2.5

\*Mass water vapor = 600mg, regardless of duration; mass dry air per cylinder = 31.6g.

Table 18. Water vapor and air masses collected from leakage and the test gas.

No. of Cylinders	Room Temperature and RH	A	B	C	D
		---Water Gained From--- Leak (mg)	Test Gas (mg)	----Air Gained From--- Leak (g)	Test Gas (g)
0.7	19°C	$6.9 \times 10^{-5}$	600	$4.91 \times 10^{-5}$	22.1
1	10% RH	$9.8 \times 10^{-5}$	600	$7.02 \times 10^{-5}$	31.6
10		$98 \times 10^{-5}$	600	$70.2 \times 10^{-5}$	316
40		$392 \times 10^{-5}$	600	$280 \times 10^{-5}$	1264
100		$980 \times 10^{-5}$	600	$702 \times 10^{-5}$	3160
0.7	28°C	$69 \times 10^{-5}$	600	$4.91 \times 10^{-5}$	22.1
1	60% RH	$98 \times 10^{-5}$	600	$7.02 \times 10^{-5}$	31.6
10		$980 \times 10^{-5}$	600	$70.2 \times 10^{-5}$	316
40		0.039	600	$280 \times 10^{-5}$	1264
100		0.098	600	$702 \times 10^{-5}$	3160

Table 19. Relative systematic error in mixing ratio from leakage,  
for runs of various lengths.

No. of Cylinders	Room Temperature and RH	E	F	Error (parts/10 <sup>4</sup> ) [(F-E)/E] x 10 <sup>4</sup>
		"True" Mixing Ratio (mg/g)*	Observed Mixing Ratio (mg/g)+	
0.7	19°C	27.14932	27.14926	-0.02
1	10%RH	18.98734	18.98730	-0.02
10		1.898734	1.898733	-0.01
40		0.4746835	0.4746856	+0.04
100		0.1898734	0.1898761	+0.14
0.7	28°C	27.14932	27.14929	-0.01
1	60%RH	18.98734	18.98733	+0.01
10		1.898734	1.898761	+0.14
40		0.4746835	0.4747133	+0.63
100		0.1898734	0.1899040	+1.61

\*Column B/D, Table 18

+Columns (A+B)/(C+D), Table 18



Table 20. Summary of maximum errors (parts per  $10^4$ ).

No. of Cylinders	Nominal Mixing Ratio (mg/g)	3 x SD	Errors in M, $\rho$ , V	Incomplete Water Absorption	Leakage
0.7	27.1	$\pm 8.1$	$\pm 2.09$	-0.017	-0.02
1	18.9	$\pm 8.1$	$\pm 2.09$	-0.025	-0.02
10	1.89	$\pm 8.1$	$\pm 2.09$	-0.25	+0.14, -0.01
40	0.475	$\pm 8.1$	$\pm 2.09$	-0.99	+0.63
100	0.189	$\pm 8.1$	$\pm 2.09$	-2.5	+1.61

Table 21. Error band in mixing ratios .

No. of Cylinders	Mixing Ratio (mg/g)	Error Band (parts/ $10^4$ )
0.7	27.1	-10.2 to +10.2
1	18.9	-10.2 to +10.2
10	1.89	-10.4 to +10.3
40	0.475	-11.2 to +10.8
100	0.189	-12.7 to +11.8

Table 22. The percentage difference between  $r_w$  and  $r_g$

-0.30% ( $T_{-20}$ , $\Delta t_0$ , $P_2$ , $F_{10}$ )	+0.10% ( $T_0$ , $\Delta t_5$ , $P_5$ , $F_{10}$ )	+0.10% ( $T_{25}$ , $\Delta t_{15}$ , $P_1$ , $F_{10}$ )
+0.17%, -0.32% ( $T_{-20}$ , $\Delta t_5$ , $P_1$ , $F_5$ )	+0.09% ( $T_0$ , $\Delta t_{15}$ , $P_2$ , $F_5$ )	+0.08% ( $T_{25}$ , $\Delta t_0$ , $P_5$ , $F_5$ )
-0.12% ( $T_{-20}$ , $\Delta t_{15}$ , $P_5$ , $F_1$ )	-0.14% ( $T_0$ , $\Delta t_0$ , $P_1$ , $F_1$ )	+0.09%, +0.22% ( $T_{25}$ , $\Delta t_5$ , $P_2$ , $F_1$ )

Table 23. The correlation of parameter levels with the percentage difference between  $r_w$  and  $r_g$

$T_{-20}$ d 0.23%	$\Delta t_{15}$ d 0.10%	$P_5$ d 0.10%	$F_{10}$ d 0.17%
$T_0$ 0.11%	$\Delta t_5$ 0.18%	$P_2$ 0.18%	$F_5$ 0.17%
$T_{25}$ 0.12%	$\Delta t_0$ 0.17%	$P_1$ 0.18%	$F_1$ 0.14%

Table 24. Experimental Errors

Saturator		Estimated Systematic Errors		3 $\sigma$ -Random Errors		$\frac{\Delta e_w}{e_w}$	$\frac{\Delta P_s}{P_s}$	$\frac{\Delta f^a}{f}$	Quad <sup>b</sup> $\frac{\Delta r_w}{r_w} \times 100$ (%)
Temp. (°C)	Press. (Pa)	Temp. (°C)	Press. (Pa)	Temp. (°C)	Press. (Pa)				
-20	2 x 10 <sup>5</sup>	0.030	69.0	0.00042	41.4	0.00293	0.00055	0.00085	0.31
-20	1 x 10 <sup>5</sup>	0.030	69.0	0.00048	47.6	0.00293	0.00117	0.00045	0.32
-20	1 x 10 <sup>5</sup>	0.030	69.0	0.00045	18.6	0.00293	0.00088	0.00045	0.31
-20	5 x 10 <sup>5</sup>	0.030	69.0	0.00033	24.8	0.00293	0.00019	0.00210	0.36
0	5 x 10 <sup>5</sup>	0.010	69.0	0.00012	33.1	0.00073	0.00020	0.00160	0.18
0	2 x 10 <sup>5</sup>	0.010	69.0	0.00009	9.0	0.00073	0.00039	0.00065	0.11
0	1 x 10 <sup>5</sup>	0.010	69.0	0.00009	16.5	0.00073	0.00086	0.00035	0.12
25	1 x 10 <sup>5</sup>	0.010	69.0	0.00033	22.8	0.00060	0.00092	0.00015	0.11
25	5 x 10 <sup>5</sup>	0.010	69.0	0.00012	24.8	0.00060	0.00019	0.00088	0.11
25	2 x 10 <sup>5</sup>	0.010	69.0	0.00018	8.3	0.00060	0.00039	0.00038	0.08
25	2 x 10 <sup>5</sup>	0.010	69.0	0.00042	18.6	0.00060	0.00044	0.00038	0.08

<sup>a</sup>Enhancement factor uncertainties obtained from Hyland's paper [31].<sup>b</sup>Combined by quadrature, i.e., the square root of the sum of the squares.

Table 25. The estimated maximum uncertainty of the generator's mixing ratio for the designated levels of the tested parameter

$T_{-20}$	0.33%	$\Delta t_{15}$	0.19%	$P_5$	0.22%	$F_{10}$	0.20%
$T_0$	0.14%	$\Delta t_5$	0.19%	$P_2$	0.15%	$F_5$	0.21%
$T_{25}$	0.10%	$\Delta t_0$	0.18%	$P_1$	0.22%	$F_1$	0.16%

Table 26. NBS Two-Pressure Humidity Generator, Mark 2, Range and Accuracy

Humidity parameter	Range	Accuracy <sup>a</sup>
Mixing ratio, $r_w$ (g water vapor/kg dry air)	$0.0005 \leq r_w < 0.0015$	3.0% of value
	$0.0015 \leq r_w < 0.005$	1.5% of value
	$0.005 \leq r_w < 0.1$	1.0% of value
	$0.1 \leq r_w < 0.3$	0.5% of value
	$0.3 \leq r_w < 515$	0.3% of value
Volume ratio, $V$ (ppm)	$1 \leq V < 3$	3.0% of value
	$3 \leq V < 10$	1.5% of value
	$10 \leq V < 170$	1.0% of value
	$170 \leq V < 500$	0.5% of value
	$500 \leq V < 820,000$	0.3% of value
Dew-point temperature, $T_d$ °C	$-80 \leq T_d < -70$	0.2
	$-70 \leq T_d < -35$	0.1
	$-35 \leq T_d < +80$	0.04
Relative humidity, RH (%) at test chamber temperature $T_c$ (°C) of:		
$-55 \leq T_c < -40$	3-98	1.5
$-40 \leq T_c < -20$	3-98	0.8
$-20 \leq T_c < 0$	3-98	0.4
$0 \leq T_c < +80$	3-98	0.2

<sup>a</sup>The estimated bounds to systematic error plus three times the standard deviation.





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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)  The National Institute of Standards and Technology (NIST), formerly National Bureau of Standards (NBS), provides a service to Government agencies and the public for the calibration of humidity measuring instruments. Calibrations are performed by subjecting the instrument under test to atmospheres of known moisture content produced by the NBS two-pressure humidity generator. The most accurate calibrations are made with the NBS standard hygrometer, a device based on the gravimetric method.  This internal report documents the original work of A. Wexler and R. W. Hyland for the NBS standard hygrometer and of S. Hasegawa for the NBS two-pressure humidity generator. The operations, tests, calibrations of component parts, and sources of errors of the standard hygrometer and the humidity generator are summarized. The random and systematic errors affecting the overall accuracy of the standard hygrometer and the humidity generator are analyzed and shown by tables.					
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